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FOREWORD

The marine environment – understanding and protecting for the future were at the forefront of the International Symposium on Marine Pollution convened in Monaco from 5 to 9 October 1998, as one of the major events of the UN International Year of the Oceans. The symposium was hosted by the Principality of Monaco on the occasion of the 150th anniversary of the birth of Prince Albert 1st of Monaco, "the Navigator Prince", one of the world's leading pioneers in oceanographic studies. The symposium was organized by the International Atomic Energy Agency, co-sponsored by the Intergovernmental Oceanographic Commission (IOC) of UNESCO, the United Nations Environment Programme (UNEP), the International Maritime Organization (IMO) and the Commission Internationale pour l'Exploration Scientifique de la Mer Mediterranée (CIESM). The new premises of the Marine Environment Laboratory in Monaco were officially inaugurated during the week of the symposium. Over 400 international experts from 61 Member States and 8 international organizations delivered 114 oral presentations in plenary and parallel sessions and made 215 poster presentations. New achievements were reported in identifying the sources of pollution, on the behaviour and fate of contaminants in seawater, biota and sediments, on the use of radioactive and non-radioactive tracers for studies of transport and circulation processes in the world's oceans and seas, on studies of radioactive waste dumping sites and nuclear weapons test sites, on local, regional and global computer modelling of the transport of contaminants and on many other topics in marine pollution. New developments in high sensitivity analytical measurements of contaminants with emphasis on nuclear and isotopic methods were also presented. Information on global and regional marine pollution studies programmes was given and participants had the chance to interact with leading experts in the field and to discuss future trends in marine pollution studies.

A ministerial meeting of the Black Sea countries organized in the framework of the IAEA TC Regional Project RER/2/003 — Marine Environmental Assessment of the Black Sea Region — was also held during the first three days of the symposium. Environmental ministers signed the Black Sea Declaration, an important document for future collaboration in the region. The Declaration stresses the important role the IAEA plays in assisting Member States in the Black Sea region by upgrading their capabilities for the assessment of the marine environment.

This TECDOC contains some of the papers submitted on issues falling within the thematic scope of the symposium which were presented in oral and poster presentations. The papers are in one of the two working languages, English or French. Several papers presented orally at the symposium have been submitted by the authors for publication in a Special Issue of the journal "The Science of the Total Environment", published by Elsevier.

EDITORIAL NOTE

CONTENTS

IAEA-SM-354/7

TEMPORAL VARIATIONS IN PLUTONIUM AND AMERICIUM INVENTORIES IN THE NORTHWESTERN MEDITERRANEAN SEA AND THEIR RELATION TO VERTICAL PARTICULATE FLUX

XA9951888

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Abstract

Temporal changes in $^{239+240}$Pu and ^{241}Am inventories in the western Mediterranean have been examined by making high resolution water column sampling and direct measurements of the vertical flux of particle-bound transuranics using time-series sediment traps. Water column profiles of both radionuclides showed well-defined sub-surface maxima ($^{239+240}$Pu between 100-400 m; ^{241}Am at 100-200 m and 800 m). Time-series measurements of $^{239+240}$Pu indicated a shift in the depth of the sub-surface maxima which appeared to be related to a change in depth of the core of low-salinity Levantine Intermediate Water. Total water column inventories for the western basin compared with total fallout inventories for the same area show that by 1990, approximately 56% of the $^{239+240}$Pu and 20% of the ^{241}Am deposited in the basin still resided in the water column. Time-series measurements of the downward flux of particulate $^{239+240}$Pu and ^{241}Am compared with transuranic removal rates derived from observed total water column inventory differences over time, show that particles sinking out of deep waters (1000-2000 m) could account for 26-72% of the computed total annual $^{239+240}$Pu loss and virtually all of the ^{241}Am removal from the water column. Computed upper water column (0-200) residence times were 20-30 y for $^{239+240}$Pu and 5-10 y for ^{241}Am in the open waters of the northwestern Mediterranean. A comparison with data for the north Pacific Ocean indicate that $^{239+240}$Pu residence times are shorter and those for ^{241}Am much longer in open waters of the northeast Pacific. ^{241}Am/$^{239+240}$Pu activity ratios in unfiltered sea water from the western Mediterranean which are six times lower than those in the north Pacific indicate the existence of a mechanism for enhanced scavenging and removal of ^{241}Am from Mediterranean waters. It is proposed that frequent atmospheric inputs of aluminosilicate particles transported by Saharan dust events could enhance geochemical scavenging and removal of ^{241}Am to the sediments of the western Mediterranean basin.

1. INTRODUCTION

One of the main objectives of oceanic flux studies is to examine spatial and temporal variability of the downward vertical transport of key elements and radionuclides involved in marine biogeochemical cycles. Two long-lived transuranic elements, plutonium and americium, have entered the marine environment as contaminants primarily via fallout from atmospheric weapons testing. The different chemical behaviours of these artificial radionuclides in sea water have made them unique tools for studying various particle-related processes in the ocean [1-4].

As a result of increasing interest in such anthropogenic tracers, a substantial database has accrued on the distribution and behaviour of plutonium and americium in sea water, suspended particulates and sediments. However, direct measurements of the particle-associated vertical flux of plutonium and americium remain rare, even though such information is essential for quantifying their residence times and removal rates in the water column [3-5]. Another method for deriving the downward

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*Present address: Lawrence Livermore National Laboratory, Univ. of California, Livermore, CA 94550, USA movements of surface-introduced transuranic elements is to compare sea water radionuclide inventories for given depth intervals over different periods of time. Based solely on sea water profiles measured in the mid-1970s and early 1980s, it has been postulated that the association of transuranics with sinking particles is responsible for the slow downward displacement of dissolved plutonium and americium reported for Mediterranean waters [2]. In order to refine such critical comparisons, we have measured high resolution depth profiles of plutonium and americium in the northwestern Mediterranean basin during a series of cruises in 1989-90. The profiles were taken at two offshore stations where time-series sediment trap experiments were also underway to quantify the present downward vertical flux of transuranium nuclides and other elements.

2. METHODS AND MATERIALS

2.1 Sea water profiles

Unfiltered sea water samples were collected during three separate cruises at two locations in the northwestern Mediterranean basin. During May and November 1989, two sampling cruises were undertaken at the French DYFAMED station (43°25'N, 07°53'E) located approximately 30 nautical miles southeast of Cap Ferrat, France. On each occasion sea water was collected at 17 depths by casts employing 30 l Niskin bottles mounted on a Rosette sampler. Approximately 60 l of sea water was taken at each depth to a maximum depth of 2250 m. In May 1990 during the 'CYBELLE' cruise, 19 depths were sampled by taking similar casts down to a depth of 2470 m at the EROS-2000 'ETRO' station (41°57'N, 05°56'E) in the Gulf of Lions approximately 60 nautical miles south of Toulon, France.

2.2 Particle fluxes

Automated time-series sediment traps were used to collect sinking particles at both stations during various periods between June 1988 and July 1990. At the DYFAMED station from June 1988 to December 1989, traps moored at 100, 200, 1000 and 2000 m collected material for time intervals ranging from 14 to 27 days. In spring-summer of 1990 sediment traps were moored at the EROS 2000 'ETRO' station in the Gulf of Lions at depths of 200, 500, 1000 and 2000 m. Each of the six collection cups sampled a consecutive 13-day period between 14 April and 1 July 1990. Trap design, sample preservation methodology and protocols for treatment and preparation of the particulate samples are described in detail elsewhere [7].

2.3 Radionuclide analysis

Unfiltered sea water samples were acidified with HNO_3 to pH 1, spiked with appropriate yield determinants (^{242}Pu and ^{243}Am), and the transuranium nuclides carried down by an $Fe(OH)_3$ precipitation. The precipitate was subsequently dissolved and $^{239+240}$Pu and ^{241}Am chemically separated and purified by methodologies described previously [1,6]

Freeze-dried particulate samples from the sediment traps (20-110 mg dry) were ground to a fine powder in an agate mortar. Aliquots were then spiked with yield determinants, digested in a concentrated HNO_3-$HClO_4$ mixture and evaporated to dryness. Any siliceous residue remaining after the initial dissolution was further treated with HF until a clear solution was obtained. All samples were subsequently taken to dryness, brought to volume with dilute HNO_3 and co-precipitated with $Fe(OH)_3$. The separated and purified $^{239+240}$Pu and ^{241}Am from the particulates were electrodeposited onto stainless steel discs and measured by alpha spectrometry using silicon barrier detectors.

3. RESULTS AND DISCUSSION

3.1 Transuranium profiles and inventories

Concentration profiles for the radionuclides are shown along with the ^{241}Am/$^{239+240}$Pu activity ratios in Figure 1. All three high resolution profiles of $^{239+240}$Pu show a distinct sub-surface maximum in concentration. The DYFAMED Nov. 1989 and EROS plutonium profiles are quite similar in shape with sub-surface maxima evident between 100-400 m. The May 1989 profile at the DYFAMED site was somewhat different from that taken at the same station six months later in that during May the sharp sub-surface maximum was centered at 100 m, whereas in November 1989 it had shifted to a depth of 400 m. The sub-surface plutonium maximum in November was observed at the same depth as the salinity maximum (38.57 PSU; Fig. 1) which closely reflects the depth of the core of Levantine Intermediate Water in this region. During May of the same year, the salinity at 100 m (38.49 PSU; Fig. 1) was much higher than that measured during November (38.13 PSU) and most likely was responsible for the maximum $^{239+240}$Pu levels observed at the same depth in May. This feature, which has been observed previously, is generally attributed to the downward vertical transport and subsequent mineralization of plutonium-enriched organic particulates which release the radionuclide back into the water column. While such a biogeochemical mechanism is probably of primary importance in maintaining the presence of this feature in the upper water column, the temporal data from the DYFAMED station indicate that hydrodynamic changes in water mass distribution in the northwestern Mediterranean may influence its exact positioning in the upper 400 m.

The ^{241}Am profile shows two sub-surface maxima, a smaller one between 100-200 m that corresponds to the Pu sub-surface maximum and a much sharper maximum centered at 800 m depth (Fig. 1). The significance of the deep sub-surface maximum is not clear but may be related to enhanced scavenging of ^{241}Am by particles at this depth; however, whatever the process involved, it does not affect the corresponding vertical distribution of $^{239+240}$Pu.

Interpretation of these profiles would be greatly facilitated by knowledge of how the concentrations have changed at various depths in the water column over time. To do this, historical data prior to 1989 from the entire western Mediterranean were assembled and inventories for various depth intervals computed. Most of the earlier profiles were comprised of very few sampling depths, which limits the accuracy of determining water column inventories; therefore, only two deep water column profiles, which were taken very near our 1989-90 stations and included at least 7 sample depths, were selected for purposes of detailed inventory comparisons.

The $^{239+240}$Pu inventories based on measurements made to at least a depth of 2000 m show that very little decrease in total inventory (~2 Bq m^{-2}) had occurred during roughly the decade over which the measurements were made. However, $^{239+240}$Pu inventories in the lower 1000-2000 m depth interval of the 2000 m water column have clearly increased over that time interval. Computations indicate whereas in the 1976-82 time frame only 33% of the $^{239+240}$Pu water column inventory resided within the lower 1000 m depth interval, by 1989-90 the percentage had increased to 46%. With the increase in deep water plutonium inventories, there was a concomitant decrease of approximately 35% in the upper mixed layer (0-200 m) during this time. These data show that plutonium is slowly being removed from the surface layers and accumulating in the deeper waters of the western Mediterranean.

Inventories in different depth intervals were constructed and compared with a detailed ^{241}Am profile taken in the northwestern basin nearly 14 years earlier [1]. The data show that the depth distributions of ^{241}Am are more complex than those of plutonium. Except in the upper mixed layer (0-200 m), there has been a clear decrease in the inventories over time. The entire 2000 m water column inventories indicate that there was roughly a 24% decrease in ^{241}Am during the period 1976-

90. Nevertheless, the fraction of that inventory residing in the deeper 1000-2000 m depth interval was the same (~56%) at both times. Thus, whereas $^{239+240}$Pu has shown a slow increase in the amount retained in the lower half of the 2000 m water column over this time period, the corresponding ^{241}Am data suggest a rapid transfer from the water column, most probably into the sediments.

These transuranic inventories deal only with the measured concentrations within the upper 2000 m of the water column in the western Mediterranean. However, nearly one half of the surface area of this region is represented by depths greater than 2000 [8], thus, any realistic computation of total transuranic inventories for the western Mediterranean must include inventories for these depths. In order to estimate inventories at depths greater than 2000 m, the cumulative inventories for $^{239+240}$Pu and ^{241}Am at each station were plotted and were found to increase linearly with depth; therefore, inventories below this depth were derived by extrapolation of this relationship.

$^{239+240}$Pu inventories to depth were determined in this fashion for three separate time periods, i.e. 1976, 1981-82 and 1989-90. The cumulative inventories in different depth intervals were then multiplied by the areas of those depth intervals in the western Mediterranean basin to arrive at estimates of the total water column transuranic inventory for each time period. In the case of ^{241}Am, profile data for the western basin are fewer, hence, a comparison of total water column inventories has only been made using the measured inventories from only two stations. The differences in total water column inventories of $^{239+240}$Pu and ^{241}Am over time and the computed mean annual loss of these radionuclides from the water column are given in Table 1. From this assessment it is evident that a greater fraction of the ^{241}Am inventory has been removed from the water column over the years than for $^{239+240}$Pu.

From known deposition rates in the northern hemisphere and observed ^{241}Am/$^{239+240}$Pu ratios in soil samples [9,10], it can be calculated that total integrated $^{239+240}$Pu and ^{241}Am delivery by 1990 was 54.3 and 20.1 TBq, respectively. Comparing the total water column inventories for 1989-90 with the total delivery values indicates that 56% and 20% of the deposited $^{239+240}$Pu and ^{241}Am, respectively, were still present in the water column at that time.

3.2 Vertical Fluxes

Concentration of both radionuclides in the sinking particulate matter were similar at the two stations ranging from approximately 0.3 to 8 Bq kg^{-1}. The ^{241}Am/$^{239+240}$Pu ratios in the particles were all higher than were observed in bulk sea water, and some very high ratios (1.9 - 2.4), more typical of Mediterranean sediments [11] were recorded in particles fluxing through 2000 m.

During the course of the 2½ month EROS experiment from April to July, the $^{239+240}$Pu concentrations in particles at 200 m steadily increased from 1.92 - 8.45 Bq kg^{-1}. Corresponding ^{241}Am levels varied by a factor of 10 throughout this period but did not follow the same increasing trend as $^{239+240}$Pu. Both ^{241}Am concentration and flux increased with depth suggesting enhanced scavenging of the radionuclide throughout the water column. Preferential scavenging of ^{241}Am relative to $^{239+240}$Pu is also reflected in the increasing ^{241}Am/$^{239+240}$Pu ratio in the sinking particles with depth. The maximum fluxes of both $^{239+240}$Pu and ^{241}Am coincided with the period of maximum sedimentation indicating that mass flux was the main factor controlling transuranic flux. These fluxes measured at both stations were similar to those recorded in the same region off Corsica during spring 1986 [3] but they were an order of magnitude lower than $^{239+240}$Pu and ^{241}Am fluxes measured in the high sedimentation regime of the Lacaze-Duthiers Canyon in the Gulf of Lions [4]. Clearly, variations in the flux of these radionuclides largely depend on the sedimentation rate.

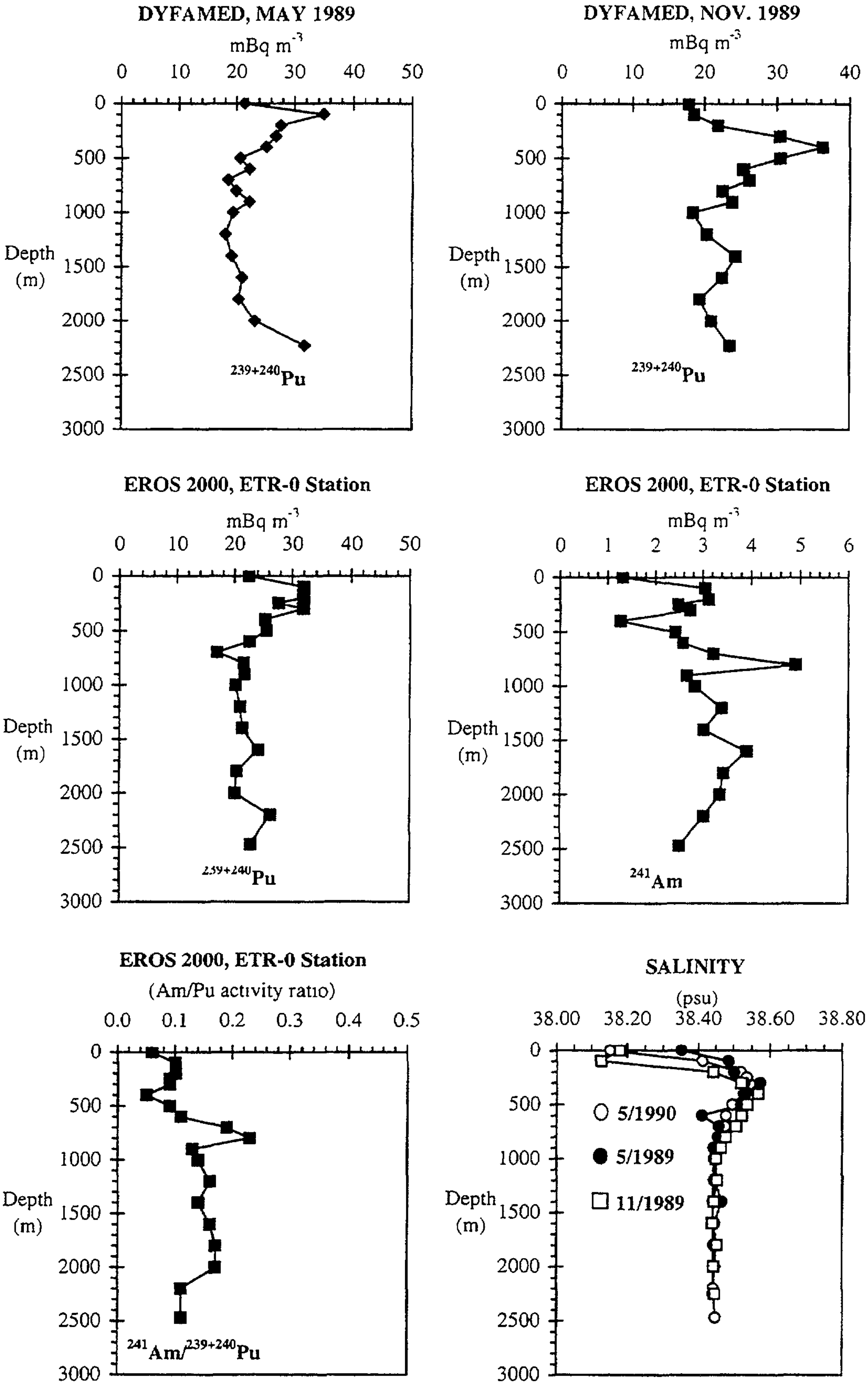

FIG. 1. Vertical profiles of $^{239+240}$Pu (DYFAMED & EROS 2000 stations), ^{241}Am (EROS 2000) and salinity (both stations) measured during 1989-90 in the northwestern Mediterranean Sea.

The degree to which large particle transport is responsible for the removal of $^{239+240}$Pu and ^{241}Am from the water column can be examined by comparing measurements of mean annual transuranic fluxes, particularly those in deep waters, with the estimates of changes in total water column plutonium and americium inventories over time (Table 1). Comparing these deep water (1000-2000 m) particulate transuranic fluxes in the open waters of the western basin (0.10 - 0.28 for $^{239+240}$Pu; 0.10 - 0.22 for ^{241}Am) with the derived annual loss rates suggests that from 26-72% of the estimated plutonium loss can be accounted for by the sinking out of large particles, whereas virtually all of the ^{241}Am removed could have occurred by this mechanism.

TABLE I. SUMMARY OF WATER COLUMN INVENTORIES (TBq) FOR TRANSURANICS IN THE WESTERN MEDITERRANEAN SEA AND MEAN ANNUAL TRANSURANIC LOSS (Bq $m^{-2}y^{-1}$) DERIVED FOR DIFFERENT TIME INTERVALS

		$^{239+240}$Pu	^{241}Am
Inventory for years			
	1976 (T_1)	34.1 TBq	5.19 TBq
	1981-82 (T_2)	33.2 TBq	-
	1989-90 (T_3)	30.3 TBq	3.95 TBq
Inventory decrease between years			
	T_2-T_1	0.9 TBq	-
	T_3-T_2	2.9 TBq	-
	T_3-T_1	3.8 TBq	1.24 TBq
*Mean loss per year for different time intervals			
	T_2-T_1	0.24 Bq $m^{-2}y^{-1}$	-
	T_3-T_2	0.53 Bq $m^{-2}y^{-1}$	-
	T_3-T_1	0.41 Bq $m^{-2}y^{-1}$	0.13 Bq $m^{-2}y^{-1}$
Overall mean loss		0.39 Bq $m^{-2}y^{-1}$	0.13 Bq $m^{-2}y^{-1}$

- The difference in inventories between any two-year intervals is computed as the inventory decrease divided by the total surface area of the western Mediterranean basin ($681 \times 10^9 m^2$) divided by the average time interval between the years when measurements were made (i.e. 5.5, 8 or 13.5 years).

The average $^{239+240}$Pu and ^{241}Am flux through 200 m during the two-and-a-half month EROS-2000 study was 0.688 and 0.273 mBq $m^{-2}d^{-1}$, respectively. Transuranic concentration profiles in sea water measured at this site during early May resulted in corresponding radionuclide inventories above 200 m of 5.9 and 0.53 Bq m^{-2}. Such fluxes would result in a residence time for $^{239+240}$Pu and ^{241}Am in the upper mixed layers of approximately 24 and 5.3 y, respectively. These residence times are considerably longer than those (2.5 and 0.14 y, respectively) reported for a 17-day deployment in the Lacaze-Duthiers Canyon [4] and are therefore more representative of average transuranic flux in open waters of the northwestern Mediterranean. Mean upper layer (0-200 m) residence times of $^{239+240}$Pu and ^{241}Am have been computed for various areas in the northwestern Mediterranean and were found to be approximately 5-10 years for ^{241}Am and 20-30 years for $^{239+240}$Pu.

Comparison of transuranic residence times in the Mediterranean with those derived from north Pacific Ocean data shows that the residence times for $^{239+240}$Pu in the Pacific were shorter than those measured at the open Mediterranean stations. Comparable data for ^{241}Am are fewer; nevertheless, in oligotrophic waters of the north Pacific gyre station, the ^{241}Am residence time (37 y) is roughly twice as long as that of $^{239+240}$Pu which is the opposite of that observed in the western Mediterranean. Thus, it appears that the biogeochemical behaviour of these fallout radionuclides in the upper water column of oligotrophic waters from these two open ocean regions is quite different. An examination of ^{241}Am/$^{239+240}$Pu ratios measured in a variety of unfiltered sea water samples from the two oceans demonstrates that ratios in western Mediterranean waters are on average some six times lower than those in the north Pacific. Such a large impoverishment of ^{241}Am relative to $^{239+240}$Pu in Mediterranean sea water points to a mechanism for effecting much more rapid removal of ^{241}Am from Mediterranean waters. It is proposed that the frequent atmospheric inputs of massive amounts of aluminosilicate particles to the Mediterranean via Saharan dust storms furnishes a particle type for which ^{241}Am has a greater binding affinity than $^{239+240}$Pu which, in turn, leads to higher vertical transport rates relative to $^{239+240}$Pu in the Mediterranean, and higher ^{241}Am transport in general compared to that in the open north Pacific.

Acknowledgements

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RADIOACTIVE TRACERS IN THE BLACK SEA: AN OVERVIEW

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Abstract

The use of radionuclides in the study of physical, chemical, biological and geological processes *in the Black Sea is discussed. A range of natural and man-made radionuclides are examined. Examples* are taken from work at WHOI and from a variety of other international laboratories working in this area. An emphasis is given to those studies which are related to recent and ongoing IAEA activities in this region. Radionuclides which originated from the Chernobyl nuclear power station accident in 1986 are highlighted, given the proximity of the Black Sea to direct Chernobyl fallout and further inputs from riverine born radionuclides from the accident site.

1. INTRODUCTION

The Black Sea is of great interest to a wide variety of scientists and policy makers due to the unique biogeochemical conditions of this basin and the large anthropogenic stresses in this region. The Black Sea is unique biogeochemically, given that it is the world's largest anoxic basin. Surface waters, which are brackish and strongly influenced by the major river inflows in the Northwest, are separated from the deep anoxic waters by a sharp density gradient. This pycnocline severely limits mixing between the upper and lower layers, and thus sets up the conditions needed for maintaining the permanent deep water anoxia. Anthropogenic influences are significant, given the large populations that live within the watershed of the Black Sea, and hence influence local and regional fluxes of materials to this basin.

The use of radionuclides in the study of physical, chemical, biological and geological processes in the Black Sea is discussed. A range of natural and man-made radionuclides are examined. Examples are taken from work conducted by our own lab at WHOI and from a variety of other international laboratories working in this area. An emphasis is given to those studies which are related to recent and ongoing IAEA activities in this region. Radionuclides which originated from the Chernobyl nuclear power station accident in 1986 are highlighted, given the proximity of the Black Sea to direct Chernobyl fallout and further inputs from riverine born radionuclides from the accident site.

In using radionuclides as in-situ tracers of physical, chemical, biological or geological processes, one needs to know as background information, something about the radionuclide source functions and the chemical behavior of the element of interest. Broadly speaking, in oceanographic studies, radionuclides are grouped into either the "conservative" or "particle-reactive" elements. Conservative tracers are used to follow physical mixing and diffusion process in the waters of the Black Sea. Particle-reactive tracers are used to study the vertical settling of sediments, biota and associated elements from the surface to deep waters and their accumulation on the seafloor.

2. RESULTS AND DISCUSSION

As an example of a successful application of a conservative tracer in the Black Sea, a time-series analysis of the penetration of Chernobyl derived ^{137}Cs and ^{134}Cs into the deep waters is presented in Fig 1.

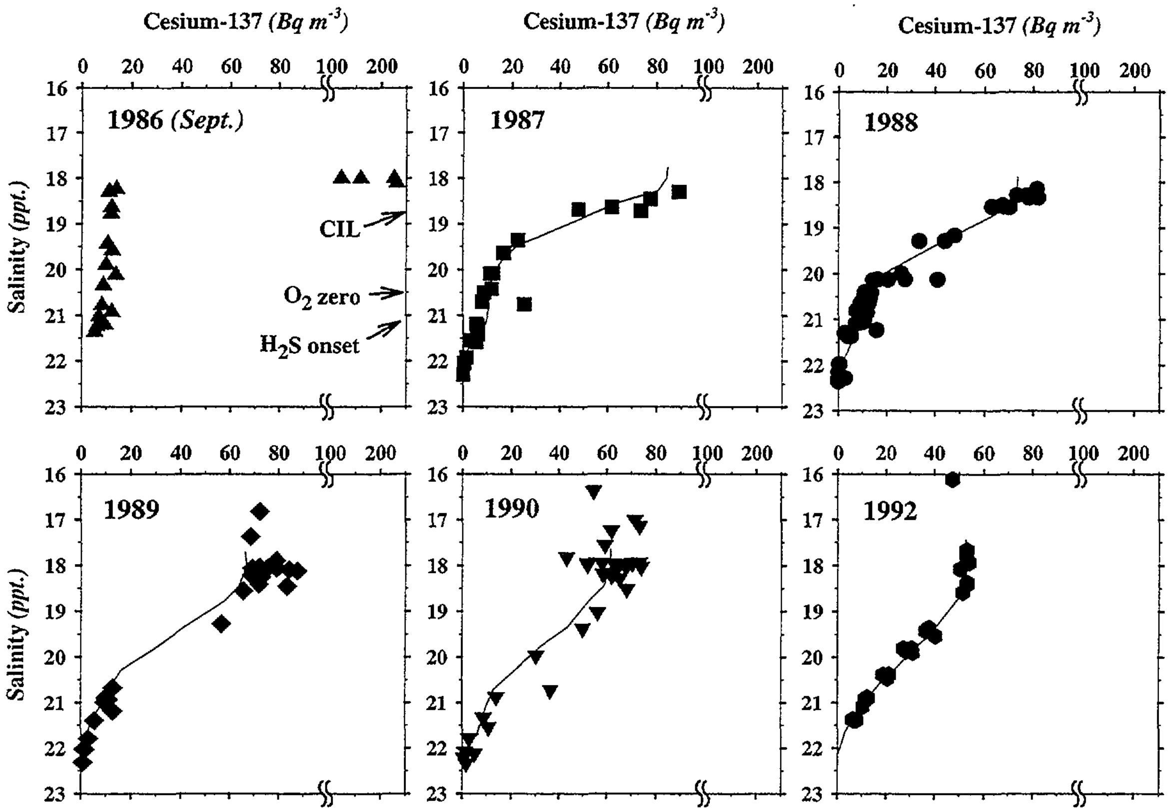

FIG 1. Time-series profiles of total cesium-137 in the Black Sea from 1986 – 1992 (adapted from [3]. Data are plotted on salinity normalized "depth" scale, and the characteristic salinities associated with the cold-intermediate layer (CIL), oxygen <5 umole (O_2 zero) and the onset of hydrogen sulfide >5 umol (H_2S onset) are identified in the 1986 panel. Note the elevated surface water Cs post Chernobyl in 1986. With time, this signal is mixed below the oxic/anoxic interface. Enhanced subsurface Cs was found in 1987 and 1988 at stations near the Bosporus where entrainment process mix surface waters rapidly to depth (see [1] for details). The solid line is the model output predicted by Staneva et al. [2].

Qualitatively, the presence of Chernobyl derived Cs below the oxic/anoxic interface (between 100 - 500 m in the central basin) only 1 year after the accident, has led to a re-evaluation of our understanding of Black Sea ventilation and entrainment processes [1,3]. The rates of mixing in this case can be evaluated though numerical modeling of the time-series evolution of this tracer, and an example of this is shown in Figure 1, where time-series data are compared to a model predicted ^{137}Cs profiles [2]. Contour plots from the model output comparing 1988 and 1992 tracer fields, demonstrates the rapid mixing of Chernobyl Cs below the pycnocline, especially along the southern margin of the Black Sea (Fig. 2).

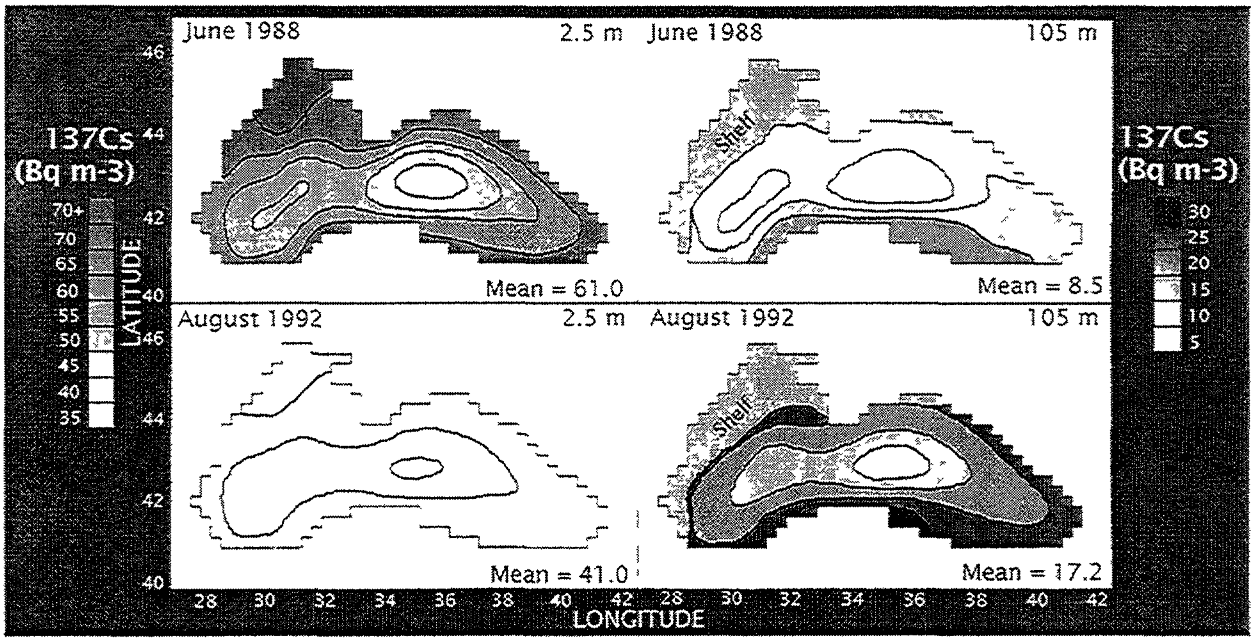

FIG 2. The model of [2] is used to predict the penetration of Chernobyl Cs between June 1988 and August 1992 at a depth of 2.5m and 105m. Note that the natural doming of the isopycnal surfaces in the Black Sea leads to lower activities at equivalent depths in the central gyres. Mean Chernobyl Cs activities at 2.5m are predicted to have decreased from 61 to 41 Bq m^{-3}, and increased at 105m from 8.5 to 17.2 Bq m^{-3} between 1988 qne 1992. These results are consistent with the measured data shown in Fig. 1.

Particle-reactive tracers have been used in the Black Sea to follow sedimentation processes. Characteristic of the particle-reactive elements is their rapid removal from surface waters and their accumulation in the underlying sediments. The anoxic bottom waters exclude the major benthic macrofauna which in most oceans serve to mix or perturb the sediment record. In the Black Sea, the sediment radionuclide record can be finely resolved, and hence the deposition history of a wide range of elements is accurately recorded in this basin's sediments. An example of the ^{210}Pb, ^{137}Cs and ^{239,240}Pu record from a core collected in 1988 in the deep western basin is shown in Fig. 3.

From such records, it was deduced that the white and black laminae characteristic of deep Black Sea sediments are not deposited annually and that accumulation rates averaged 70 g m^{-2} yr^{-1} [4].Also, given the anoxic conditions, many elements exist in alternate redox states which can significantly change their removal rates. For plutonium, the reduced forms dominate below the oxic/anoxic interface (Fig. 4).

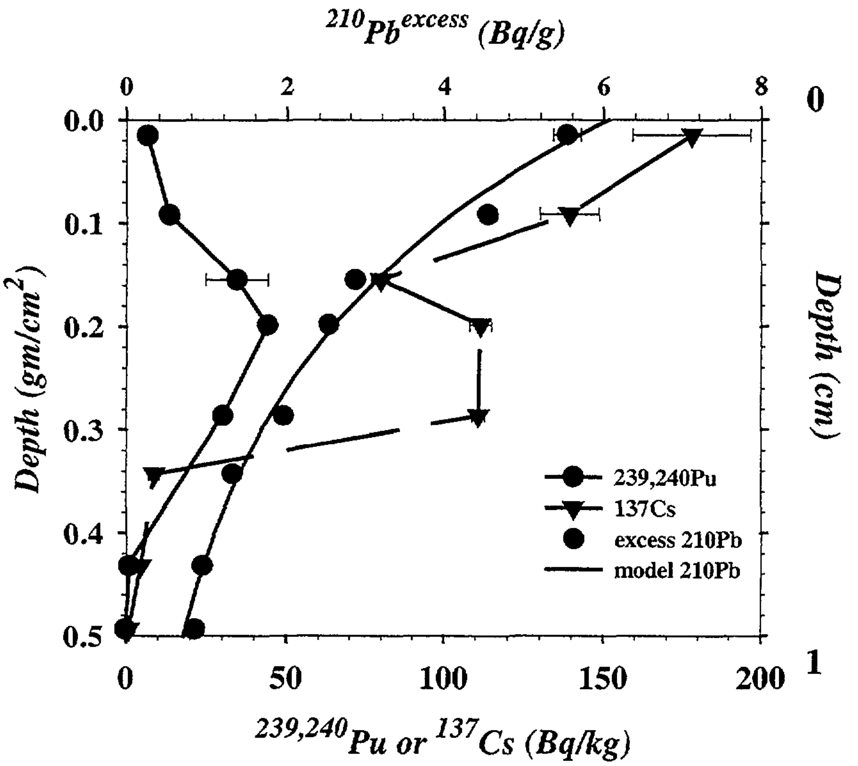

FIG 3. Sediment profiles of excess ^{210}Pb, ^{137}Cs and $^{239,240}Pu$ from a core collected in 1988 in the deep western basin [4]. The line through the 210Pb data is an exponential fit to a constant accumulation model which predicts an accumulation rate of 70 g m^{-2} yr^{-1}. The subsurface peaks in Pu and Cs at a depth of roughly 0.5 cm are due to weapons testing fallout which peaked in the early 1960's. The surface elevation of Cs is due to Chernobyl derived Cs delivered to the Black Sea after the accident in 1986.

These low redox conditions lead to a very high efficiency of plutonium removal from the watercolumn, compared to the rest of the worlds oceans [5].

3. SUMMARY

In summary, there are a number of important questions concerning the water balance, pollution loading, and fate of materials dumped into the Black Sea that can be addressed using radiotracers. These applications are quite interesting scientifically, as the Black Sea is a unique environmental setting for making these measurements. These radionuclides act as in-situ tracers which can be used to quantify the rates of many natural and/or anthropogenically altered processes. These radiotracer applications are quite relevant to the local communities surrounding this basin. A large number of issues related to fisheries, pollution, tourism and recreation, and resource and waste management can be better addressed through wise application of these natural and man-made radionuclides.

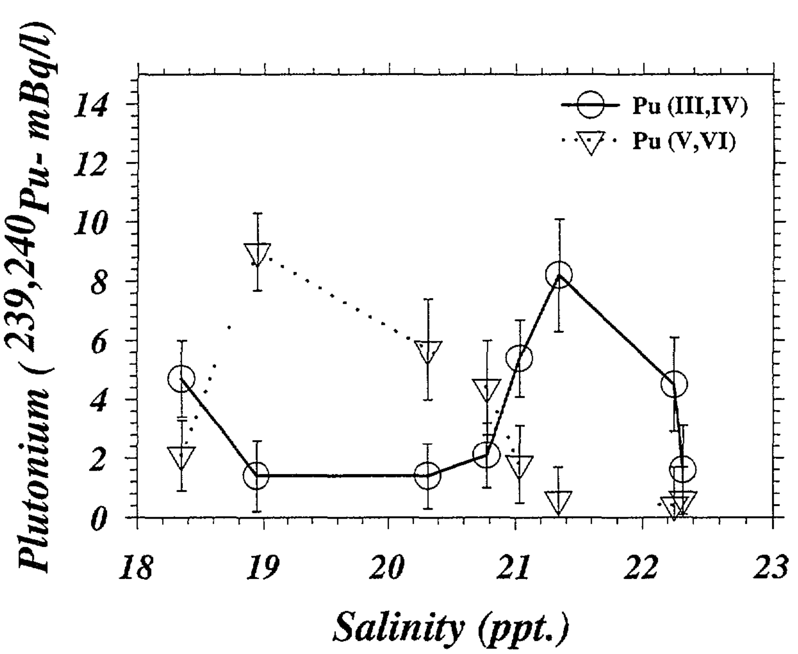

FIG 4. Salinity normalized "depth" profile of oxidized plutonium (Pu (V,VI)) and reduced plutonium (Pu(III,IV)) from the central western Black Sea in 1988 (adapted from [5]) Note that the oxic/anoxic interface is at salinities of 20.5 to 21.0, hence there is a shift to more reduced Pu forms in the deep waters. The higher particle reactivity of reduced Pu leads to its preferential removal in near bottom waters and accumulation in the sediments, as evidenced by relatively elevated sedimentary Pu inventories (95% of the total Pu inventory is in the underlying sediments vs. 5% in water column- [3].

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TENEURS EN METAUX TRACES DES SEDIMENTS DE SURFACE DU LAC SUD DE TUNIS AVANT RESTAURATION

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Abstract

The analysis of metal (Hg , Cd , Pb, Cu ,Cr, Ni, Mn, Zn, Fe) concentrations in the surface sediments of the South Lake of Tunis before its restoration showed a high level of contamination. The values for mercury , cadmium and lead oscillate respectively between (0,17 and 2,6 µg /g d.w), (0,13 and 13,3 µg/g d. w); (3,97 and 698 µg/g d. w). This pollution is generated by the intensive industrial activity situated on south banks of the Lake. This environment constitutes since more of the millennium a outfall of urban used waters and since one century an outfall of industrial waste waters strongly charged with nutrients and heavy metals.

1. INTRODUCTION

Le Lac Sud de Tunis est une lagune située dans la région septentrionale de la Tunisie , au sud du 37 ^{ème} parallèle dans une zone caractérisée par un climat méditerranéen sec [1] .Couvrant 1120 hectares, elle faisait partie d'une étendue d'eau plus vaste ; le Lac de Tunis (5000 ha) .
Les reconstitutions archéologiques montrent que l'existence de la lagune de Tunis remonte au moins à deux siècles avant J.C [2] , il semble en être de même pour la ville de Tunis .La lagune a été divisée en 2 parties nord et sud après avoir creusé en 1885 le canal de navigation reliant le port de la Goulette à celui de Tunis. Le lac Sud communique avec la mer par deux canaux artificiels , le canal de Radès qui le relie directement au golfe de Tunis et le canal de navigation à travers les 3 brèches équipées de pêcheries fixes (figure :1). La lagune est un milieu laminaire dont la bathymétrie moyenne n'excède pas un mètre . C'est un milieu où règnent des conditions drastiques comme les fluctuations spatio-temporelles brusques et très importantes des paramètres abiotiques . En outre les échanges avec la mer sont faibles et l'hydrodynamisme est très atténué particulièrement au niveau des anses où les eaux sont quasiment stagnantes [3].Il est le siège d'une eutrophisation extrême se traduisant par des blooms alternés de phytoplancton et d'algues chlorophycées macrothalliques [4] .Il est également le lieu de crises dystrophiques estivales génératrices de conditions létales et d'apparition d'eaux colorées [4].

Ses berges sud abritent l'un des pôles industriels le plus important de la Tunisie avec 587 usines dont la majorité déverse directement les effluents bruts dans le plan d'eau, notamment dans sa partie Sud Ouest .[5],[6] et[7] .
Notre étude pluridisciplinaire constitue une contribution pour une meilleure approche de cet écosystème qui jusqu'à ce jour n'a fait l'objet que d'études fragmentaires et ponctuelles . Nos résultats serviront d'état initial et d'échelle objective pour l'évaluation du projet d'aménagement du Lac une fois réalisé. Le présent travail constitue une contribution à l'évaluation de l'état de pollution

des sédiments superficiels par les métaux traces issus des rejets industriels avant les travaux de restauration de cet écosystème.

2. MATERIEL ET METHODES

Des prélèvements saisonniers de sédiments de surface ont été effectués durant les années 1995-1997 au niveau de 15 stations géoréférencées (figure :1) réparties sur l'ensemble du Lac en tenant compte à la fois de la distribution géographique (centre du Lac , zone des émissaires , zone sous influence marine ..) et des diverses conditions écologiques du milieu (qualité physico-chimique des eaux , biodiversité faunistique et floristique ..).Les sédiments de surface (10 cm) ont été prélevés à la benne , traités et analysés par Spectrophotométrie d'Absorption Atomique à flamme air/acétylène ou à four en graphite [8].Pour établir des comparaisons avec les travaux antérieurs [9] ,[10] , [11] , nous avons été amené à analyser la fraction totale des sédiments .

3. RESULTATS ET DISCUSSIONS

Les résultats des analyses montrent d'une manière générale que le niveau de contamination des sédiments de surface du Lac est élevé pour tous les métaux étudiés (tableau1) en particulier pour les teneurs en Mercure total (figure 2), en Cadmium (figure 3) , en Plomb (figure 4) , en Chrome (figure 5) et en Cuivre (figure 6).

Les concentrations en métaux lourds toxiques diffèrent, toutefois, selon les secteurs avec une dissymétrie d'Est en Ouest et du Nord au Sud dans la répartition de la plupart des métaux. En effet, suite au rythme accéléré d'industrialisation durant les 20 dernières années , la Tunisie s'est dotée de plus de 10000 établissements industriels localisés principalement dans les grandes agglomérations de la frange littorale[12] .Parmi ces établissements industriels, 1200 usines sont classées fortement polluantes et sont à l'origine de détériorations environnementales [12]. La région du Lac Sud compte actuellement 587 unités industrielles dont 184 établissements fortement pollueurs[12].Les berges du Lac abritent essentiellement des industries agro-alimentaires (12%) , chimiques (8%) , industries diverses (tanneries et teintureries… soit 32%) , des industries textiles , de l'habillement et du cuir (12%), des industries mécaniques, métalliques et électriques (27%) et des industries de matériaux de construction , céramique et verreries (9%)

Les concentrations critiques sont observées à l'Ouest du Lac, en effet cette région regroupe à elle seule plus de 350 industries[7] .Les principaux rejets polluants dans cette zone sont les métaux lourds, les colorants, les graisses et les huiles minérales [13].Le Lac Sud de Tunis constitue le principal milieu récepteur des effluents industriels avec seulement 13% déversant leurs rejets dans un réseau d'assainissement approprié[6].

Les teneurs les plus basses correspondent aux zones sous influence marine à l'exception de la concentration en fer anormalement élevée observée à la station 28 (tableau :1) , ceci probablement en relation avec la voie ferrée située sur le canal de Radès et servant au transport de minerai de fer depuis le nord ouest du pays jusqu'au port de la Goulette. Seuls le Fe et le Mn ont une origine naturelle, les autres métaux résultent des actions anthropiques et proviennent surtout des rejets industriels [10].

En outre, les variations sont aussi liées à la granulométrie , les sédiments du secteur Ouest étant constitués de vase fine, (fraction qui adsorbe le plus), alors que dans la zone Est dominent les sédiments sablo-coquillers.

La pollution par les métaux lourds dans le Lac connaît également une évolution spatio-temporelle.

A titre indicatif, en 1976, les teneurs extrêmes étaient moins importantes (1,43µg/g) en Mercure, (347 µg/g) en Chrome, (3,57 µg/g) en Cuivre et (93 µg/g) en Manganèse[9].
Depuis cette date avec l'évolution industrielle, les valeurs extrêmes ont doublé, voire même triplé pour certains polluants comme le Chrome, le Mercure et le Manganèse.

En raison de la véritable menace que constituent les sédiments contaminés pour le Lac et le littoral proche , un plan de gestion rationnelle de leur éviction a été prévu dans le cadre des futurs aménagement et restauration de la qualité environnementale du Lac. En effet toute perturbation du milieu lors des travaux peut avoir un impact catastrophique sur le Lac et les communautés le peuplant.

4 CONCLUSION

Les sédiments du Lac Sud de Tunis constituent à l'heure actuelle une formidable réserve de polluants métalliques toxiques fortement corrélés avec la nature et l'importance de l'activité industrielle le bordant .Les rejets contaminés ont fait de la lagune un écosystème très perturbé et extrêmement fragilisé

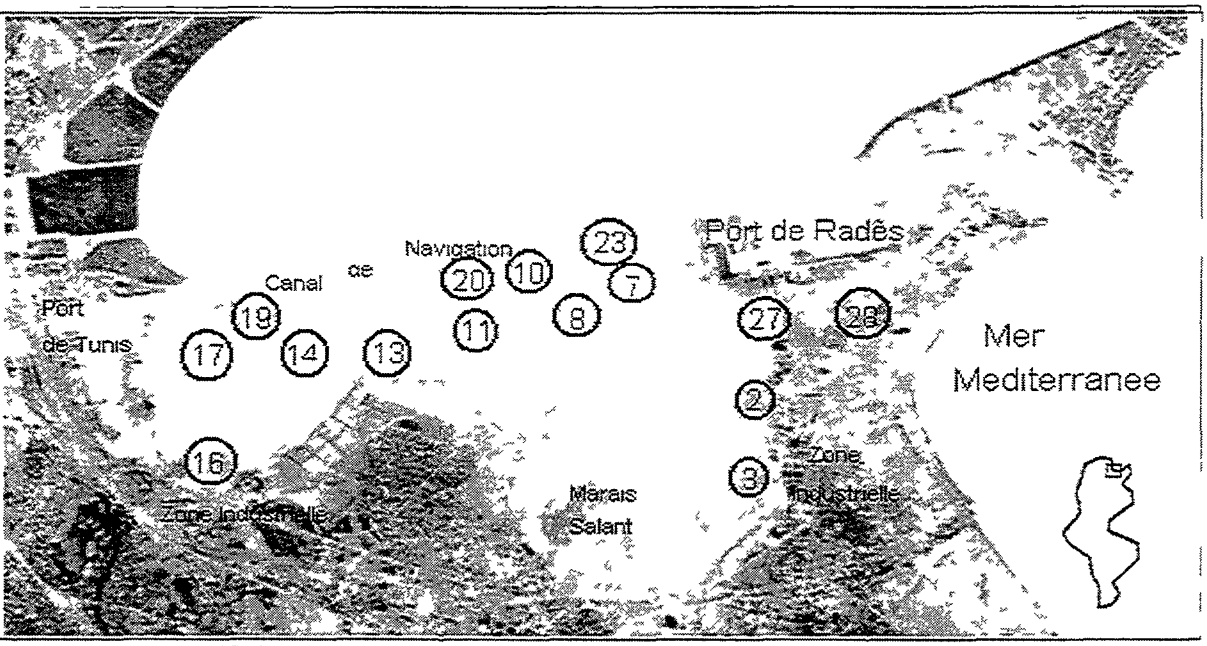


FIG.1. Situation géographique du lac et des lieux de prélèvement

TABLEAU 1 TENEURS EN METAUX TRACES DES SEDIMENTS DE SURFACE DU LAC DE TUNIS EXPRIMEES EN PPM DE POIDS SEC

Station	Coordonnees Geographiques		Hg_{Tot}	Cd	Ni	Mn	Fe	Zn	Pb	Cu	Cr
	Lat NORD	Long EST									
2	36°47',16	10°16',09	**0,27**	**0,14**	**9,6**	**65**	**2812**	**14**	**4**	**11**	**20**
3	36°46',76	10°16',09	**0,72**	**0,13**	**7,9**	**84**	**3443**	**21**	**24**	**6**	**38**
7	36°48',16	10°15',09	**0,59**	**1,92**	**24**	**119**	**18995**	**227**	**259**	**48**	**133**
8	36°47',66	10°15',09	**0,68**	**1,15**	**14,7**	**82**	**8557**	**120**	**137**	**21**	**102**
10	36°48',16	10°14',59	**0,32**	**0,14**	**8,2**	**67**	**2415**	**15**	**10**	**4**	**26**
11	36°47',66	10°14',09	**0,84**	**1,72**	**15**	**97**	**8811**	**132**	**145**	**23**	**91**
13	36°47',66	10°13',59	**1,36**	**1,15**	**10,4**	**106**	**5960**	**91**	**86**	**17**	**71**
14	36°47',66	10°13',09	**1,74**	**3,43**	**25,4**	**139**	**22725**	**425**	**545**	**75**	**296**
16	36°47',16	10°12',59	**2,6**	**13,3**	**27,1**	**135**	**20920**	**791**	**698**	**128**	**800**
17	36°47',66	10°12',59	**2**	**1,75**	**18,3**	**306**	**22139**	**144**	**124**	**290**	**81**
19	36°47',92	10°12,77	**0,48**	**1,12**	**15**	**123**	**11342**	**194**	**213**	**29**	**104**
20	36°48',06	10°14',13	**0,37**	**1,07**	**11,3**	**115**	**10019**	**158**	**141**	**20**	**63**
23	36°48',23	10°15',16	**0,31**	**0,14**	**9,6**	**93**	**5877**	**33**	**19**	**9**	**27**
27	36°47',90	10°16',30	**0,38**	**1,06**	**35,7**	**138**	**22530**	**200**	**131**	**42**	**68**
28	36°47',86	10°16',55	**0,17**	**0,82**	**21,2**	**150**	**26332**	**200**	**174**	**32**	**97**
Normes Néerlandaises relatives a la qualité des sédiments de surface (seuil d'alarme)			15	30	200	/	/	2500	1000	400	1000
Intervalles de concentrations des Sediments de surface pour la Région mediterraneenne [14]			/	0,02 a 64	/	/	/	1,7 a 6200	3 a 3300	0,6 a 1890	/

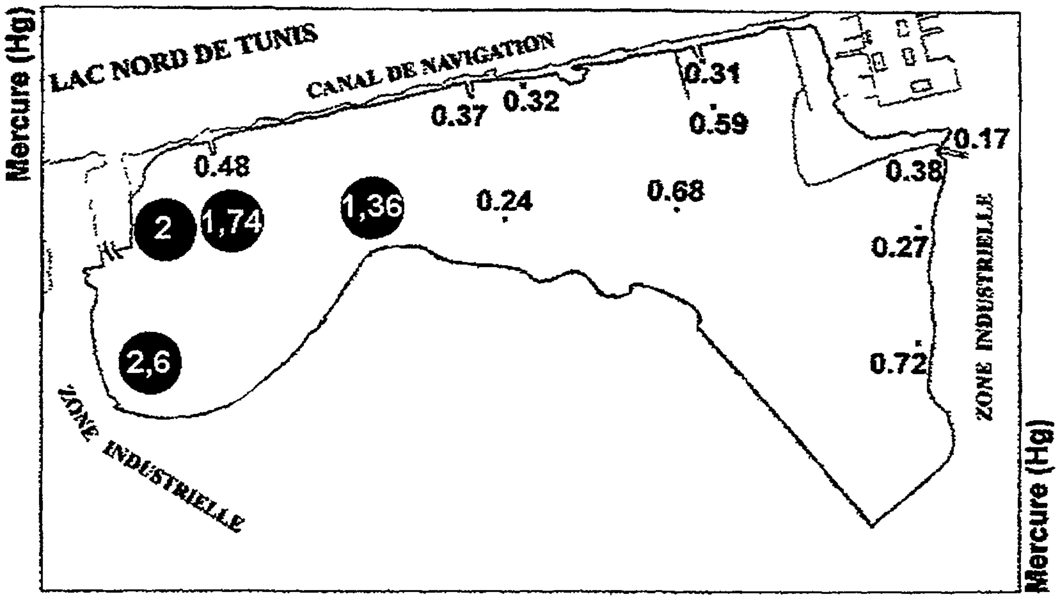
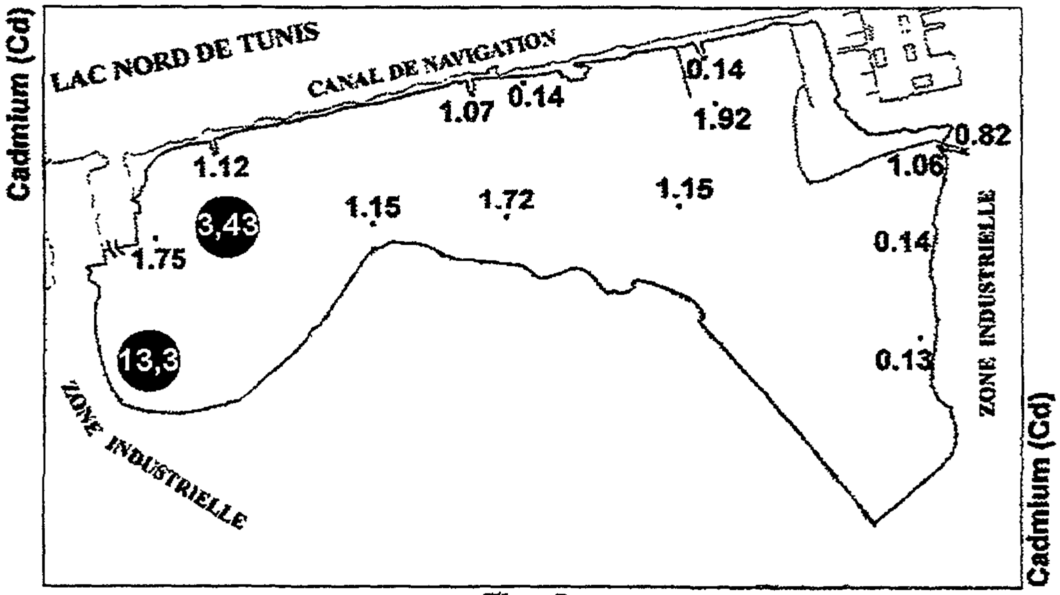


Fig : 2



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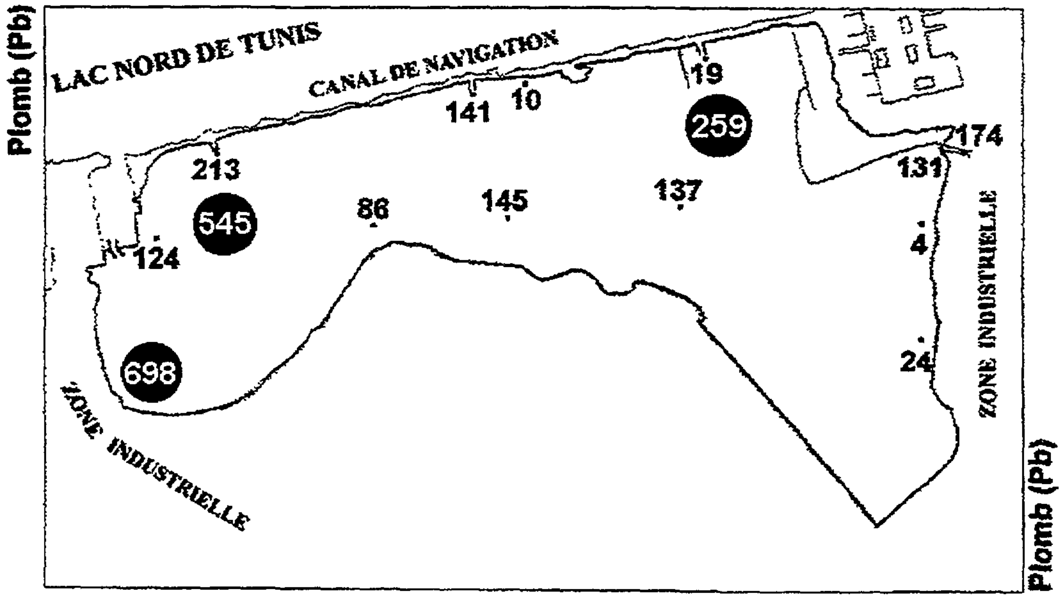

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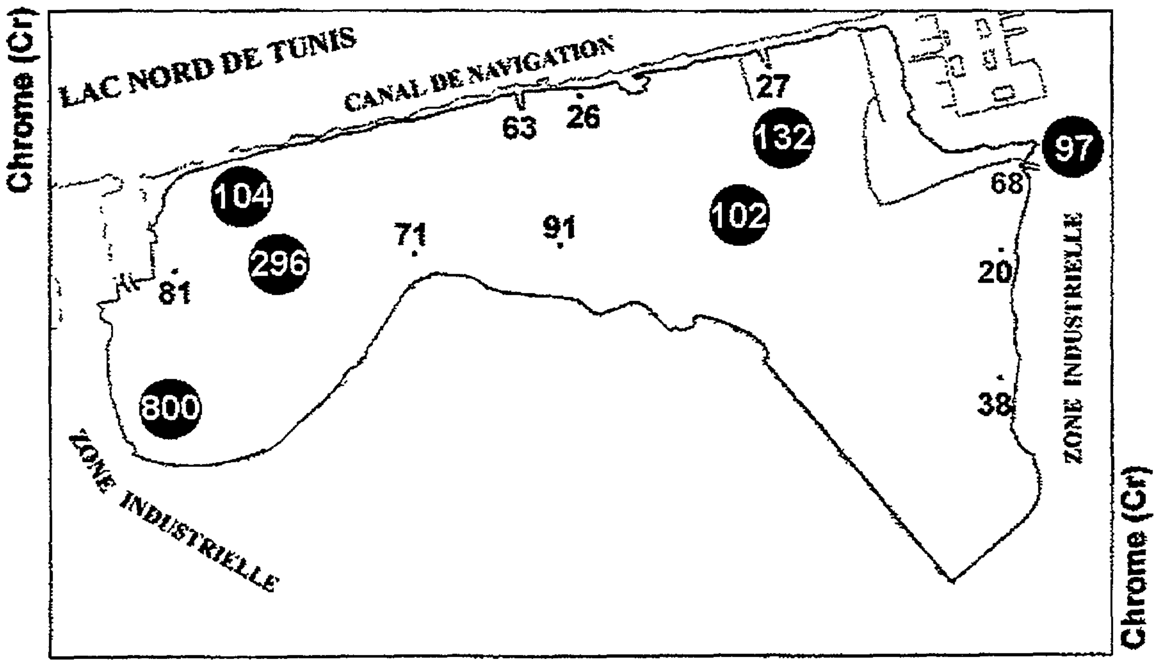

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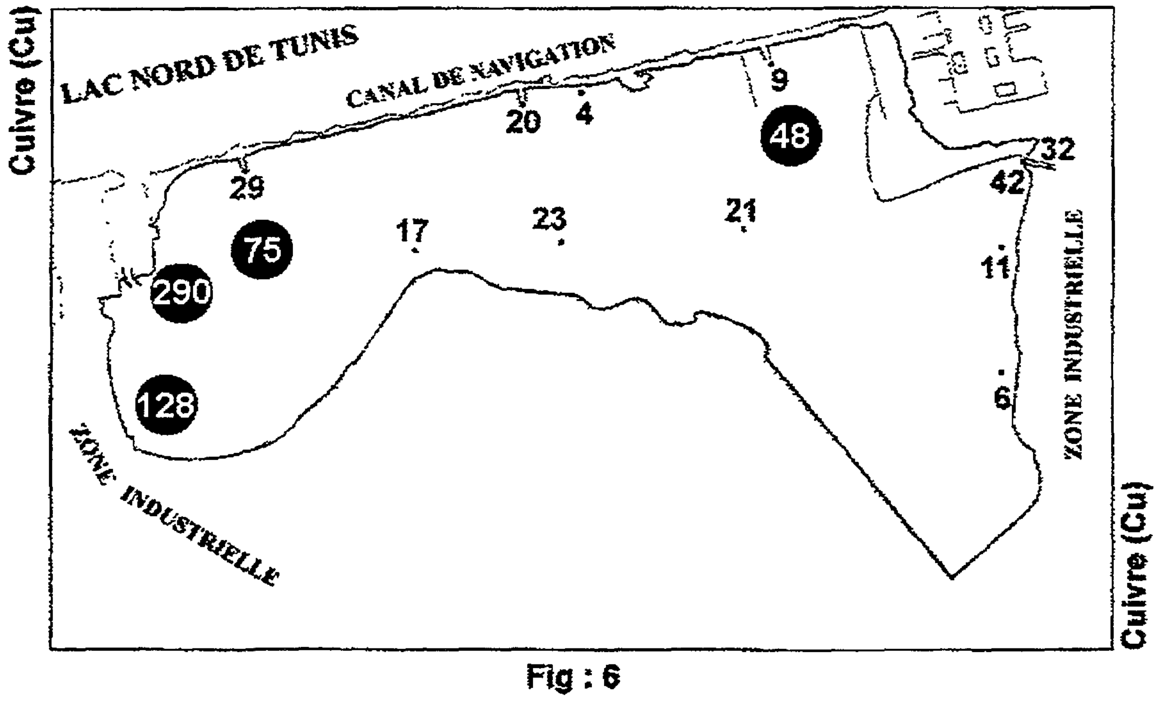

Fig : 6

FIGS. 2 à 6 Teneurs en polluants métalliques (en ppm de poids sec) des sédiments de surface du lac Sud de Tunis avant restauration

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LONG-TERM LOSS RATES OF RADIOISOTOPES OF COBALT, ZINC, RUTHENIUM, CAESIUM AND SILVER BY *MYTILUS EDULIS* UNDER FIELD CONDITIONS

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Abstract

Long-term loss rates of cobalt, zinc, ruthenium, caesium and silver by *Mytilus edulis* soft parts as well as shells were measured under field conditions in the Mediterranean Sea at Monaco during a period of 13 months after experimental contamination. For all 5 elements, the loss could be described by two exponential functions for the soft parts and one for the shells. Biological half lives for the long-lived compartment ranged from ~20 days for caesium to 100 – 200 days for cobalt, zinc, ruthenium and silver for soft parts as well as for shells. A comparison with results from similar experiments performed under very different environmental conditions in the Baltic Sea indicated that caesium and maybe silver had a faster turnover in the warm and saline Mediterranean, whereas loss rates for cobalt and zinc were comparable. It is argued, that reliable deduction of loss rates require experiments running over several months to a year, and it is pointed out that shorter term experiments – even up to 3 months – may give biased results.

1. INTRODUCTION

Mytilus edulis, the common edible mussel, is the most widely used bioindicator for various contaminants in coastal marine and estuarine waters [1,2]. It is therefore of utmost importance to have a quantitative knowledge of accumulation rates and turnover rates under realistic environmental conditions. The most convincing way of establishing "field-realistic" conditions under a long-term loss experiment is to contaminate the animals and then put them back in the sea in enclosures allowing a free exchange of seawater including food particles. During December 1987 – January 1989 we performed such an experiment in the Marine Laboratory and in the Mediterranean Sea at Monaco.

2. MATERIALS AND METHODS

The contamination of animals with radionuclides, radionuclide data and counting technique is described elsewhere [3]. The chosen animals had a uniform size (average ± SD): shell length: 40.9 ± 1.5 mm, soft parts dry weight: 0.22 ± 0.08 g. After a 9 day laboratory contamination, the initial 5 days of loss were conducted in the laboratory in running, clean Mediterranean seawater. The animals were then transferred to polypropylene cages with long slits ensuring free water circulation and suspended on a buoy system in the Monaco Marine Reserve, "Reserve Sous Marine de Larvotto". Each cage contained 10 animals. The animals were then sampled, normally one cage per sampling, at 5, 12, 19, 34, 49, 64, 91, 125, 168, 216, 259, 314, and 410 days. When sampled, the animals were separated in shell and soft parts and analysed individually. All radiotracer data are decaycorrected to the beginning of the experiment and expressed as activity per individual whole soft parts or shells.

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RESULTS

Growth and condition data are given in Fig. 1. The selected condition index, CI = g dry soft parts / (mm shell length)^3 is expected to reflect physiological oscillations during the year [4].

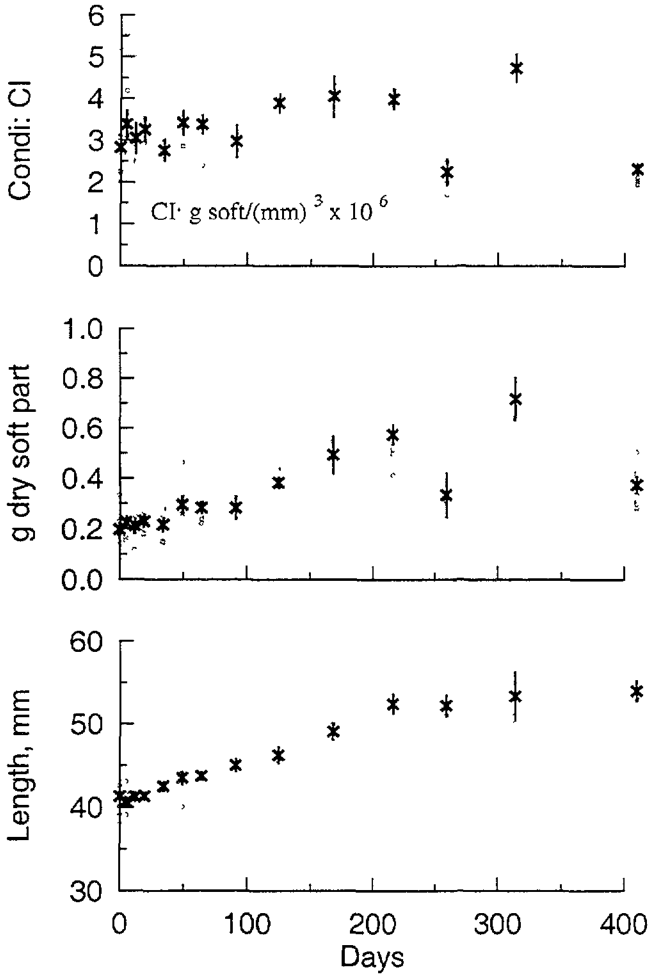

FIG. 1. Condition of Mytilus edulis during a 13 month loss experiment the Mediterranean Sea. Condition index, CI (see text), soft parts dry weight and shell length are all given for individual animals and as mean ± SE

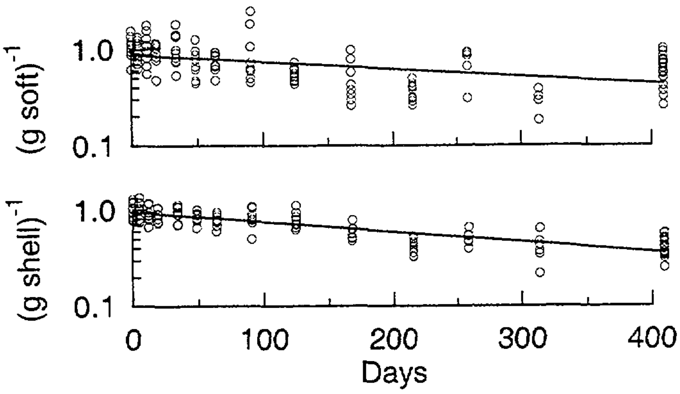

FIG. 2. Mytilus edulis. Effect of growth on contaminant concentration shown as reciprocals to soft parts dry weight and shell weight normalised to unity at time zero. Lines are exponential regressions with half time of 398 days (λ_g: -0.00174 d^{-1}) for soft parts and 290 days (λ_g: -0.00239 d^{-1}) for shells.

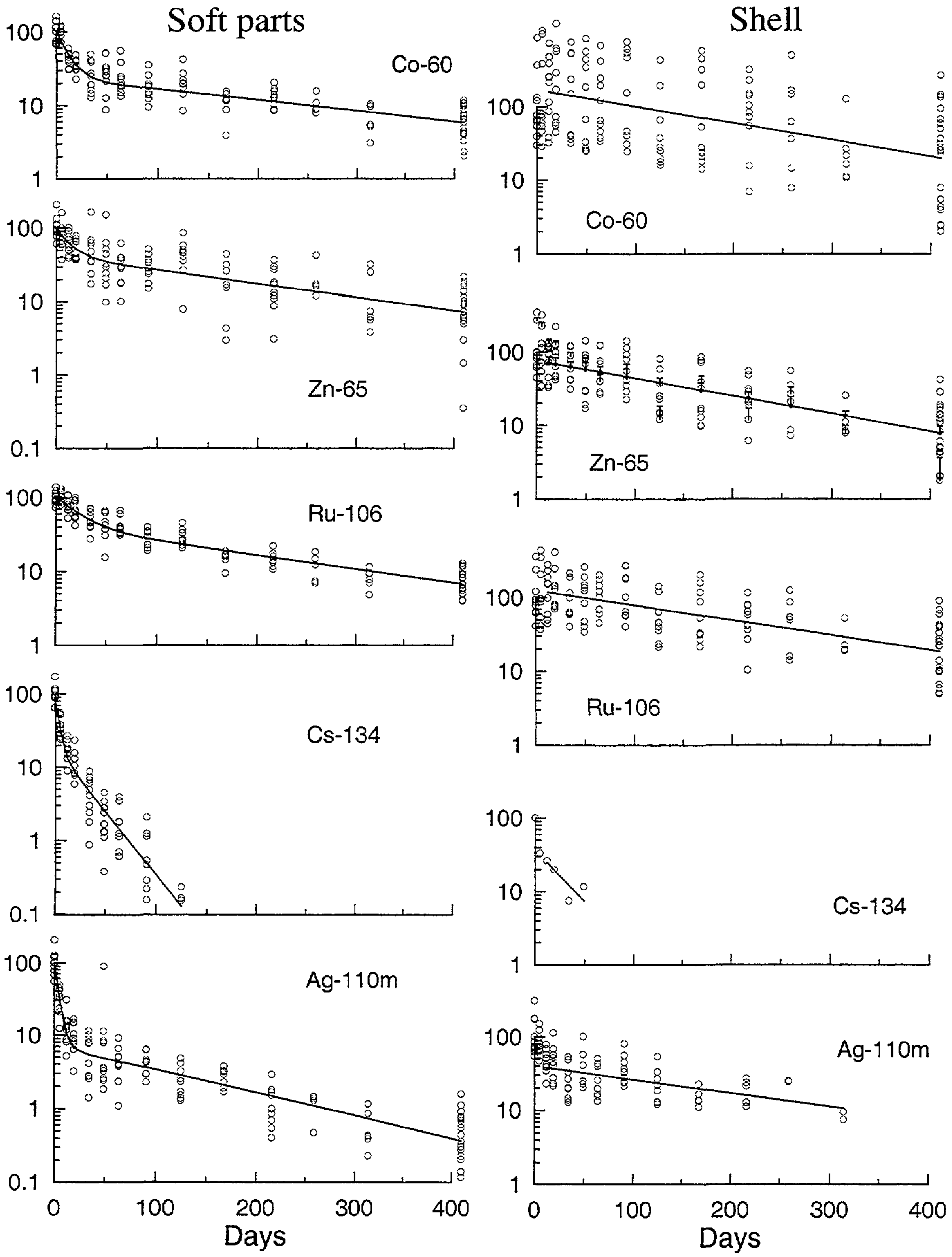

FIG. 3: Loss of cobalt, zinc, ruthenium, caesium and silver by Mytilus edulis soft parts (left column) and shell (right column) in the Mediterranean at Monaco. Results are normalised to the beginning of the loss experiment and expressed as a percentage of the average tracer content at the beginning of the loss experiment. Circles denotes individual animals, lines refer to the exponential functions given in Tables 1 and 2.

TABLE I. MYTILUS EDULIS SOFT PARTS. LOSS PARAMETERS IN 13 MONTH FIELD EXPERIMENT AT MONACO

Isotope	^{60}Co	^{65}Zn	^{106}Ru	^{134}Cs	^{110m}Ag
Fast compartment, a_1%	80	54	64	70	87
λ_{b1}, d^{-1}	-0,0946	-0,0704	-0,0408	-0,2937	-0,2577
$T_{½,b1}$, days	7,3	9,9	17	2,4	2,7
Slow compartment, a_2 %	23,5	41,4	39	17,9	6,9
λ_{b2}, d^{-1}	-0,00341	-0,00428	-0,00428	-0,03961	-0,00715
$T_{½,b2}$, days	203	162	162	18	97
λ_g, soft parts, d^{-1}	-0,00174	-0,00174	-0,00174	-0,00174	-0,00174
$\lambda_{b2}+\lambda_g$, d^{-1}	-0,00515	-0,00602	-0,00602	-0,04135	-0,00889
$T_{½,b2+g}$, days	134	115	115	17	78
$T_{½,ph}$, days	1925	244	368	754	250
$\lambda_{b2+g+ph}$, d^{-1}	-0,00551	-0,00886	-0,00790	-0,04227	-0,01166
$T_{½,eff}$, days	126	78	88	16	59

TABLE II. MYTILUS EDULIS SHELL. LOSS PARAMETERS IN 13 MONTH FIELD EXPERIMENT AT MONACO

Isotope	^{60}Co	^{65}Zn	^{106}Ru	^{134}Cs	^{110m}Ag
% of total in shell*, t=0	51 ± 21	27 ± 13	30 ± 13	3.4 ± 0.9	5.3 ± 1.7
% of total in shell*, t=410 d	71 ± 25	31 ± 23	51 ± 21	-	-
Intercept, a%	169	76	40	36	125
λ_b, d^{-1}	-0,00522	-0,00553	-0,00421	-0,03195	-0,00465
$T_{½,b}$, days	133	125	165	22	149
λ_g, shell, d^{-1}	-0,00239	-0,00239	-0,00239	-0,00239	-0,00239
$\lambda_b+\lambda_g$, d^{-1}	-0,00761	-0,00792	-0,00660	-0,03434	-0,00704
$T_{½,b+g}$, days	91	88	105	20	98
$T_{½,ph}$, days	1925	244	368	754	250
λ_{b+g+ph}, d^{-1}	-0,00797	-0,01076	-0,00848	-0,03526	-0,00981
$T_{½,eff}$, days	87	64	82	20	71

*: average ± SD

The condition index was rather stable with a slowly increasing tendency except for 259 and 410 days, where the index was lower due to lower soft parts dry weight (Fig. 1). It is not known what caused the oscillation, but obvious possibilities could be reduced water flow caused by overgrowth with newly settled mussels or algae, and reduced space in the cages due to growth. From the length data (Fig. 1) it is seen that the animals are growing steadily till day 216. Thereafter, the length seems more stable.

In the present experiment, remaining radiotracer contents is expressed as a total amount per animal. Fig. 2 gives the reciprocals to individual soft parts dry weight and shell weight normalised to unity at time zero. This gives the effect of growth on the concentration of a hypothetical constant contaminant, i.e. the "growth dilution". Exponential regression lines with half times of 398 days (λ_g: -0.00174 d^{-1}) for soft parts and 290 days (λ_g: -0.00239 d^{-1}) for shells are given, i.e. the growth alone is responsible for a dilution of contaminant levels to half the original values in 398 days for soft parts and 290 days for shells. The growth dilution of the soft parts was clearly faster in the beginning of the experiment.

The loss curves for total soft parts (Fig. 3) could be resolved in 2 exponential phases, a fast compartment with biological half lives of a few days, and a slow compartment with biological half lives of ~2 weeks for caesium and 3-7 months for silver, ruthenium, zinc and cobalt. The amount of tracer remaining in the animals (a_t) is thus described as

$$a_t = a_1 e^{\lambda_1 t} + a_2 e^{\lambda_2 t}$$

where a_1 and a_2 are percentages of the initial activity present in the two compartments, λ_1 and λ_2 are the loss rates (d^{-1}) estimated for the two compartments by sequential linear regression analysis of ln(activity) versus time, and t is time in days after the initialisation of the loss phase. Corresponding half lives are calculated for each compartment as

$$T_{1/2} = \frac{ln2}{-\lambda}$$

For the shells, loss rates (Fig. 3) could be satisfactorily described by a single exponential curve.

Tables 1 and 2 give the calculated loss data for soft parts and shells, respectively. Table 2 furthermore gives the percentage of the total radiotracer content found in the shell at the start and at the end of the experiment. For Co, Zn and Ru, the importance of the shell increased with time. The biological loss constants (λ_b) and biological half-lives ($T_{1/2b}$) describes only the loss of the applied tracer elements from the animals excluding growth dilution and physical decay of the radiotracer. When mussels are used as bioindicators, growth dilution and, for radionuclides, the physical decay, are also of importance for observed contaminant concentrations and for how suited mussels are as bioindicators. Tables 1 and 2 are therefore also giving the exponential rate constants for growth dilution (cf. Fig. 2) and for physical decay of the used radiotracers. The exponential rate constants are additive. It is therefore simple to calculate the biological half lives including growth dilution, $T_{1/2,b+g}$, and the effective half lives, $T_{1/2,eff}$, including growth dilution as well as physical decay, by simply adding the relevant rate constants and calculating the $T_{1/2}$ value from the equation above.

3. DISCUSSION

Long term biological loss rates are key components in modelling contaminant behaviour in a mussel population, and the literature contains numerous works on estimating biological half lives for the studied elements. Table 3 gives data for Mytilus soft parts from comparable long-term loss experiments under field conditions. The literature contains several other works on wholebody loss rates and on short duration loss experiments. They are not included here, whereas any further published data in the category mentioned in Tab. 3 are not omitted deliberately. The present experiment was planned to be comparable to the two Baltic experiments [5,6] in order to deduce effects of environmental differences between the Mediterranean Sea and the very different cold and low salinity Baltic environments. As the two Baltic experiments gave very different results, this was not a clear success. Probably the faster turnover of Cs in Monaco compared to Oskarshamn can be taken as a true effect of the higher salinity and higher temperature in the Mediterranean. The Oskarshamn data may in general be more comparable to the Monaco experiment, as the Forsmark environment showed a clear effect of a long and cold winter starting shortly after the contamination [5]. This may have prevented the complete purging of the fast compartments before the animals "slowed down" during the winter. In the Oskarshamn experiment, contamination started mid summer in stead of in November, and the following winter was much milder than during the Forsmark experiment. If then the present experiment is compared with the Oskarshamn experiment only, silver seems to have a faster turnover rate in the Mediterranean, whereas there are hardly any effect for cobalt and zinc. The two experiments based on transplanting field-contaminated mussels to clean environments [7,8,9] should both be comparable to the present experiment concerning full marine salinity.

It has been made likely, that long-term loss rates for cobalt and zinc are unaffected by the length of accumulation [10]. However, experimentally measured loss rates are certainly affected by the duration of the loss experiment. A reason for this is that the loss rates for soft parts is normally described by at least two exponential compartments (cf. Fig 3 and [5,6,7,8,9,10]). It is therefore not possible to deduce the long-term loss rates until the faster compartments are purged. This could be the explanation of the shorter half-lives given in Ref. [11]. It may thus be concluded, that reliable deduction of loss rates require experiments running over several months to a year, and that shorter term experiments – even up to 3 months – may give biased results.

The shell data (Table II) are not discussed here due to lack of comparable literature data.

TABLE. III. MYTILUS SOFT PARTS. LONG TERM LOSS RATES UNDER FIELD CONDITIONS EXPRESSED AS BIOLOGICAL HALF LIVES WITHOUT GROWTH DILUTION, $T_{\frac{1}{2},B}$, DAYS

Conditions during loss	Co	Zn	Ru	Cs	Ag	Ref.
Monaco, 13 months.	203	162	162	18	97	Present
Forsmark, Baltic Sea, 10 months, 5-6 ‰	79	67			45	[5]
Oskarshamn, Baltic Sea, 17 months, 7 ‰	287	158		78	∞	[6]
La Jolla, California, 12 month*		82				[7]
Plymouth, English Channel, 12 month**			261	39		[8,9]
Monaco, 3 months***	19-27	27-34			12-16	[11]

*: M. californianus, field contaminated, transplanted.**: Field contaminated near Sellafield, transplanted.
***: Laboratory contamination from food or water, respectively.

Acknowledgements

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TEMPORAL AND SPATIAL RESPONSES OF THE BIOINDICATOR *FUCUS* TO DISCHARGES OF ^{99}Tc IN THE EASTERN IRISH SEA

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Abstract

Technetium-99 is a radioactive isotope discharged under authorisation to the Irish Sea from the British Nuclear Fuels plc Sellafield reprocessing plant in Cumbria via a marine pipeline. An increase in ^{99}Tc discharges from Sellafield in recent years has provided an ideal opportunity to undertake a more detailed investigation of its environmental behaviour. Here, the temporal and spatial response of *Fucus sp.* to the increased discharges has been investigated and its role as a bioindicator assessed. Initial investigations in 1995, have confirmed the expectation that *Fucus* does act as an effective bioindicator of ^{99}Tc, with easily detectable ^{99}Tc concentrations (1 - 15 kBq kg^{-1} wet weight) being encountered, providing a time integrated signal of ^{99}Tc discharges. Analysis of subsequent samples collected during 1996, however, have shown significant short-term peaks in *Fucus* ^{99}Tc concentrations close to Sellafield (up to 90 kBq kg^{-1} wet weight) and this can be related to peaks in ^{99}Tc seawater concentrations. This type of response suggests that *Fucus* has a means of rapidly accumulating ^{99}Tc, although the rate at which this accumulated component may be eliminated remains unclear. This effect was only observed at sites close to Sellafield (within 15 km). Relatively constant ^{99}Tc concentrations in *Fucus* were found at more distant sites (50 - 150 km).

1. INTRODUCTION

Technetium-99 is a radioactive isotope ($t_{1/2}$ 213,000 years) which has been discharged under authorisation to the Irish Sea from the British Nuclear Fuels plc Sellafield reprocessing plant in increased quantities since 1994 due to the treatment of stored effluents. This radionuclide is released in a highly soluble form, which disperses rapidly from the point of discharge. Certain marine organisms found in and around the Irish Sea, including some commonly ingested by man, are known to concentrate ^{99}Tc to differing extents. Ingestion of seafood containing enhanced levels of ^{99}Tc therefore constitutes a pathway by which man can be indirectly exposed to the beta radiation emitted by this isotope. Although the effects of exposure to beta radiation are well understood, relatively little is known about the behaviour of ^{99}Tc in the marine environment. The increase in ^{99}Tc discharges from Sellafield in recent years has provided an ideal opportunity to undertake a more detailed investigation of its environmental behaviour.

The affinity of brown seaweeds for technetium has identified this type of algae as excellent bioindicators to trace the movement of technetium through the oceans. *Fucus vesiculosus* and *Ascophyllum nodosum* have been used to trace technetium released from BNFL Sellafield as far as the Baltic Sea, estimating a transit time of 4-6 years [1]. Here, the temporal and spatial response of *Fucus* to the increased discharges has been investigated and its role as a bioindicator assessed.

2. COMPLETE SELLAFIELD ^{99}Tc DISCHARGE PROFILE

The levels of ^{99}Tc discharged from Sellafield to the Irish Sea have only been accurately quantified since 1978. The lack of data prior to this date requires estimation of earlier discharge rates. The only information available in the open literature regarding ^{99}Tc discharges for 1952-1969 was published as part of the CEC project MARINA in 1990 [2], where discharges for this period were estimated at 8 TBq per annum. The discharge rate for 1970-77 was estimated from the study of ^{99}Tc concentrations in seaweed in the Baltic Sea. A transit time of four years, originally derived for the movement of radiocaesium from Sellafield to the Danish Straits, was applied to ^{99}Tc. Sellafield ^{99}Tc discharges from 1952-1996 are shown in Fig 1.

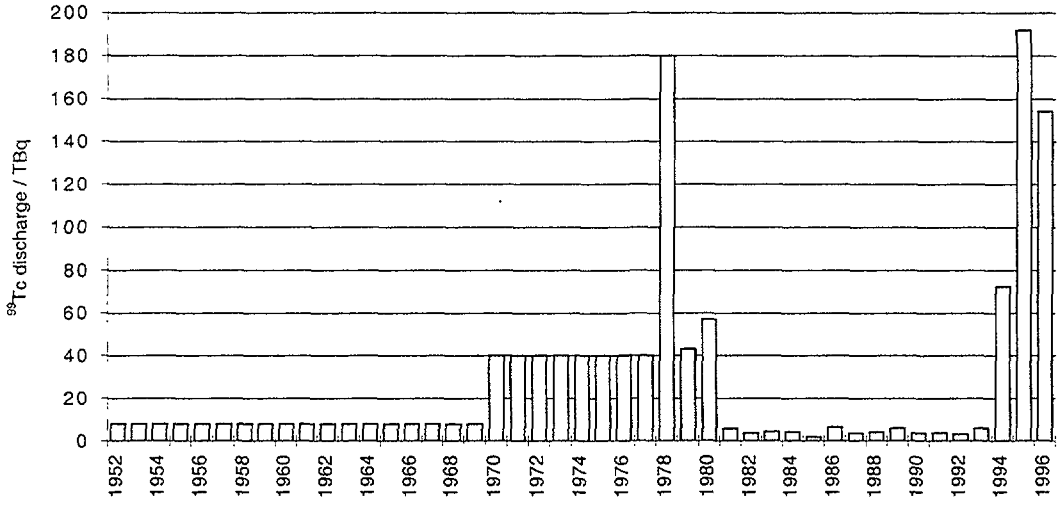

FIG. 1. Sellafield ^{99}Tc discharge profile

3. SAMPLING AND ANALYSIS

The brown algae *Fucus vesiculosus* was one of the first species identified as an indicating medium for ^{99}Tc. Despite its infrequent use as a foodstuff for man, this species was chosen for study since:

(1) much of the data available on ^{99}Tc in the marine environment deal with this species;
(2) it is geographically widespread, being a dominant species of algae found in Europe and northeast America;
(3) it often occurs as large fronds which are easy to sample.

Seaweed samples were collected from nine coastal sites from south-west Scotland, north-west England and north Wales in June 1995, February 1996 and September 1996. Seawater samples were also collected from the nine sites in September 1996. All seaweed and seawater samples were analysed for ^{99}Tc using ICP-MS with ^{95m}Tc as yield tracer [4].

Figure 2 shows the position of the nine sites relative to the Sellafield nuclear fuel reprocessing plant. The sites indicated by filled circles were visited on all three sampling trips (Stairhaven, Portling, St. Bees, Ravenglass, Fleetwood, and Colwyn Bay). The sites indicated by grey circles were only visited on the initial sampling trip (Annan, Maryport, and Hoylake). On return to the laboratory, one to two kilogrammes of fresh *Fucus* samples were cleaned and allowed to air dry before being weighed to give the sample "dry weight". The dried *Fucus* samples were ground and homogenised to a particle size of <1 mm, 10g of which was then taken for analysis.

Samples of surface seawater (1 – 2 m depth) were taken off the Cumbrian coastline at monthly intervals between March 1995 and March 1997. The samples were taken approximately 2 km offshore at Sellafield, St. Bees and Ravenglass (see Fig 2.). Seawater samples were filtered prior to processing using a high volume filtration apparatus. Particulate matter with a particle size diameter greater than 0.45 µm was removed by pumping the sample through cellulose nitrate filter papers.

4. RESULTS

4.1. ^{99}Tc in off shore seawater

^{99}Tc concentrations measured in seawater off the Cumbrian coast between March, 1995 and March 1997 are illustrated in Fig 3. ^{99}Tc seawater concentrations off Sellafield were routinely higher than those at Ravenglass, which in turn were higher than those at St. Bees. Seawater concentrations off Sellafield were found to vary over three orders of magnitude. A variation of two orders of magnitude was observed at Ravenglass, while concentrations at St. Bees remained relatively constant.

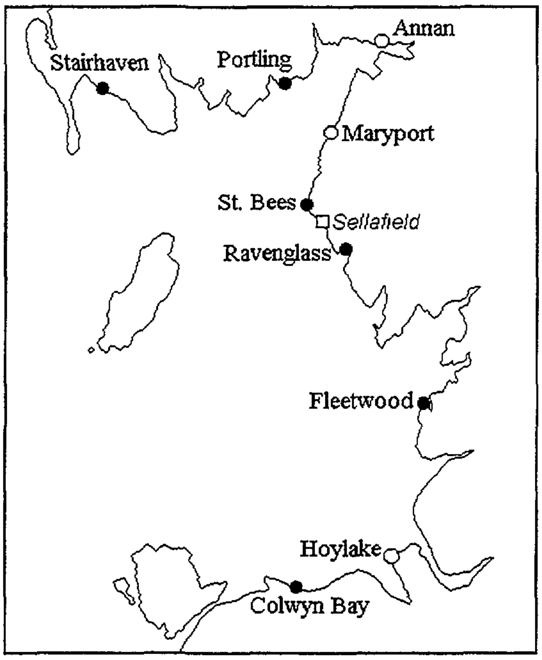

FIG. 2. Shoreline sampling sites

This variation can be attributed to the nature of ^{99}Tc discharges from Sellafield. The effluent is treated in batches, each batch taking approximately five weeks to process, with discharges to sea occurring approximately three times per week. The effluent is discharged over an eight hour period - from four hours before high tide until four hours after high tide - to ensure maximum dispersion. Since ^{99}Tc is discharged in a highly soluble form, pulsed discharges inevitably lead to pulses in seawater concentration. This effect is more pronounced closer to the discharge point and decreases significantly with increasing distance from Sellafield. The ^{99}Tc becomes increasingly dilute as it spends more time in the water column.

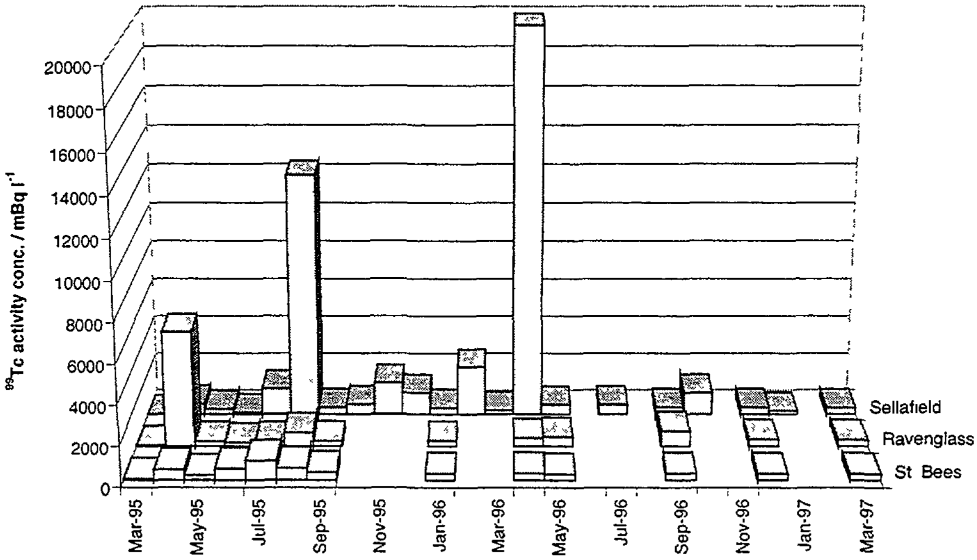

FIG. 3. ^{99}Tc in seawater off Cumbria

4.2. ^{99}Tc in seaweed

The results acquired from the three sets of shoreline sampling are illustrated in Fig 4. This shows a plot of ^{99}Tc concentration against distance from Sellafield, with the y axis representing the point of discharge. For ease of presentation, distance from Sellafield is taken as the shortest straight line distance by sea to the respective sampling sites. It is recognised that this will not represent the true distance travelled by a given discharge to the sampling site, as this movement will be directly influenced by tides, currents and winds The spatial distribution of ^{99}Tc concentrations in seaweed is similar to that described earlier in seawater samples. The highest concentrations are found closest to Sellafield and concentrations tend to decrease with increasing distance. Within this general trend, however, the data shows some specific differences. Most significantly, there appears to be substantial variation of ^{99}Tc concentrations in *Fucus* close to Sellafield.

The samples collected in June 1995 show a fairly consistent decrease in ^{99}Tc concentration with increasing distance from Sellafield. Increased activities were found at all sites in March 1996. Larger increases were found at sites to the north of Sellafield compared with the south, with the particularly large increase observed at St. Bees from 15 kBq kg^{-1} to 67.5 kBq kg^{-1}.

This peak at St. Bees was not observed in the sample taken from the same site in September 1996. The ^{99}Tc concentration had fallen from 67.5 kBq kg^{-1} to 22.8 kBq kg^{-1}, only slightly higher than the concentration observed in June 1995. In September 1996, in place of the peak concentration at St. Bees, a peak concentration was found at Ravenglass. Between March 1996 and September 1996, the ^{99}Tc concentration at Ravenglass increased from 18.4 kBq kg^{-1} to 92 kBq kg^{-1}. The north to south trend observed for ^{99}Tc concentrations in *Fucus* in September 1996 closely resembles the ^{99}Tc concentrations in seawater collected at the same time (Fig. 5). This demonstrates *Fucus* responding quickly to prevailing conditions.

Setting aside the peak concentrations in *Fucus* close to Sellafield, it is evident that concentrations measured in March 1996 and September 1996 are greater than those measured in June 1995 with the highest concentrations in general being found in the March 1996 sample suite.

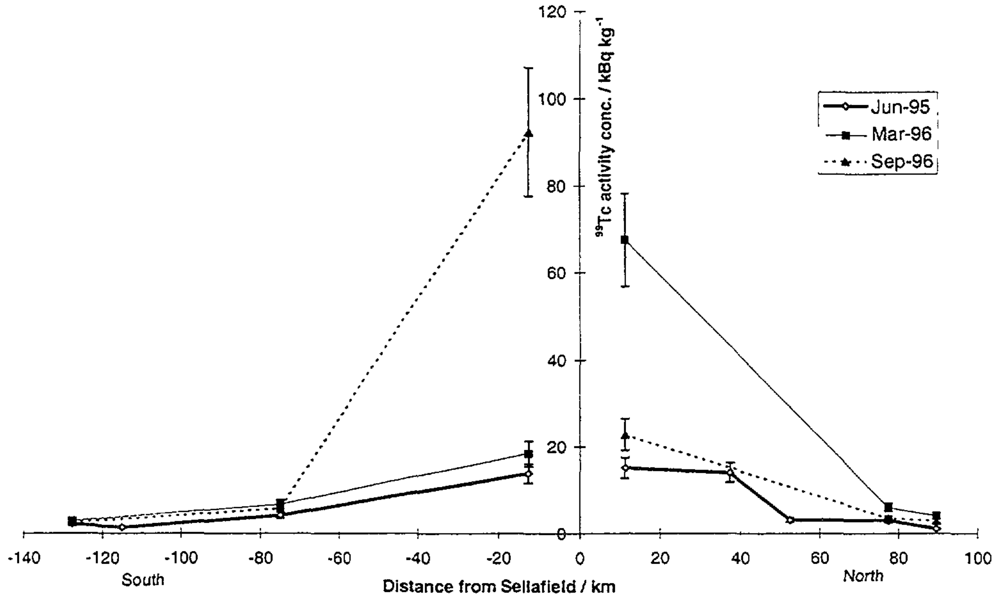

FIG. 4. ^{99}Tc in Fucus. vs. distance from Sellafield ($\pm 1\sigma$ uncertainty)

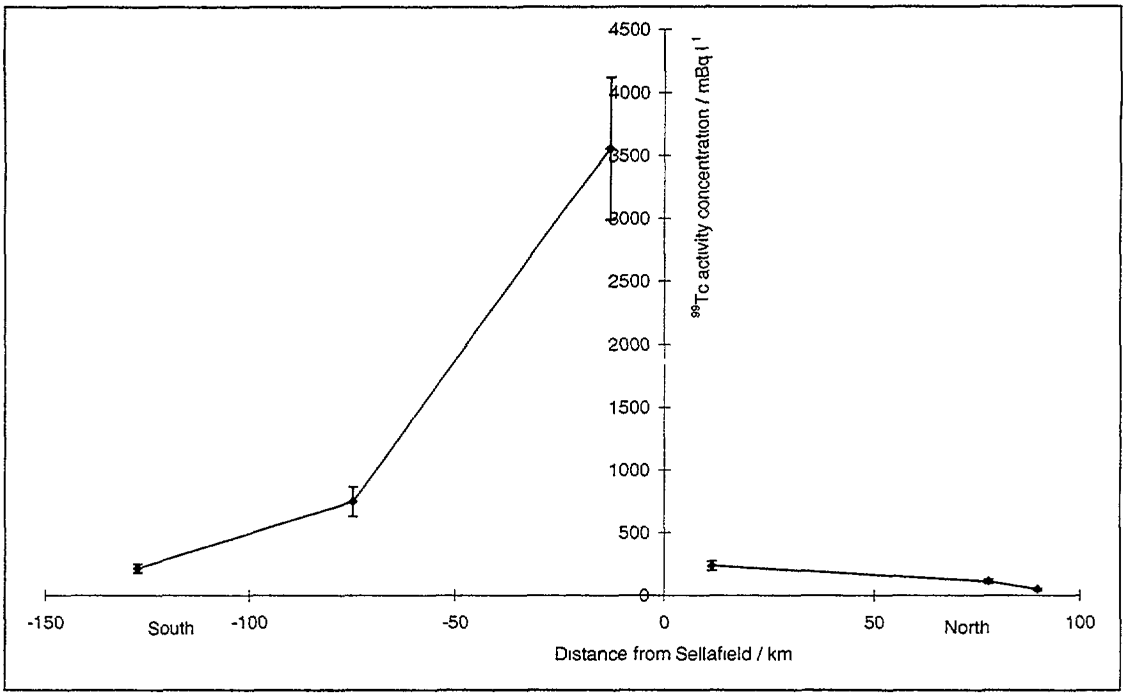

FIG. 5. ^{99}Tc in UK shoreline seawater, September 1996

The steady increase of ^{99}Tc concentrations in *Fucus* with the increased discharges from Sellafield is also illustrated by a number of other datasets, some taken at more regular intervals. The Ministry of Agriculture Fisheries and Food (MAFF) has reported *Fucus* concentrations at Sellafield in their annual reports since 1977 and from some 14 sites around the UK since 1991 [5]. McCartney & Rajendran [6] report steady increases in ^{99}Tc *Fucus sp.* concentrations at Ravenglass and Whitehaven between 1993-1995. Smith *et al* [7] describe both the spatial distribution of ^{99}Tc in *Fucus vesiculosus* around the coastline of Ireland and time-series data for Balbriggan on the western coast of Ireland between 1988 and 1996. In a more detailed examination of MAFF data after the commissioning of the Enhanced Actinide Removal Plant (EARP), Hunt *et al.* [8] observed a steady increase in ^{99}Tc concentration at St. Bees but a more variable increase at Sellafield throughout 1994-1995.

5. DISCUSSION

Although the uptake of ^{99}Tc is believed to be an active, metabolically controlled process [10, 11], rates of accumulation and elimination for *Fucus sp.* have not been reported. Laboratory studies of the kinetics in other species of brown algae, including *Sargassum vulgare* and *Cystoseira compressa*, have shown rapid accumulation of technetium [12, 13]. Concentration Factors of up to 1000 have been shown to be achieved in a matter of hours. Elimination appears to occur in two stages in all *Phaeophyta* species studied, an initial rapid loss of 30-50% occurring in the first few days followed by a more steady excretion stage with biological half lives varying between 20-200 days for different species.

If the kinetics of uptake and elimination in *Fucus sp.* are similar to those observed in other brown algae, this may account for the peaks in ^{99}Tc concentration found in this work. *Fucus* may respond rapidly to changes in ^{99}Tc concentration in their immediate environment. A large proportion of recently accumulated ^{99}Tc may be eliminated over a few days and, if subjected to reduced ^{99}Tc concentrations quite quickly, the remainder may be eliminated over a longer time period. In this case, the pattern of ^{99}Tc accumulation by the seaweed is likely to show significant peaks followed by an associated rapid reduction in concentration. If the time taken for *Fucus* to eliminate ^{99}Tc is longer than the periods between exposure to peak ^{99}Tc concentrations, then there will also be an underlying component of increasing concentration within this accumulation pattern.

Hence, initial investigations in 1995, have confirmed the expectation that *Fucus* does act as an effective bioindicator of ^{99}Tc, with easily detectable ^{99}Tc concentrations (1 - 15 kBq kg^{-1} wet weight) being encountered, providing a time integrated signal of ^{99}Tc discharges. Analysis of subsequent samples collected during 1996, however, have shown significant short-term peaks in *Fucus* ^{99}Tc concentrations close to Sellafield (up to 90 kBq kg^{-1} wet weight) and this can be related to peaks in ^{99}Tc seawater concentrations. This type of response suggests that *Fucus* has a means of rapidly accumulating ^{99}Tc, although the rate at which this accumulated component may be eliminated remains unclear. This effect was only observed at sites close to Sellafield (within 15 km). Relatively constant *Fucus* concentrations were found at more distant sites (50 - 150 km). The variation in ^{99}Tc seawater concentration at these distant sites is likely to be less extreme than at the Cumbrian coast near Sellafield.

Acknowledgements

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SHELLS OF *NERITA* GASTROPOD BIO-MONITORS OF HEAVY METAL POLLUTION AROUND THE INDIAN OCEAN

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Abstract

Minor and heavy metals Mg, Sr, Mn, Fe and Zn were measured in individual shells of four different *Nerita* species collected from Phuket Island, Thailand. Shell weight and crystallography were also recorded. Heavy metal concentrations were poorly correlated with both shell weight and crystallography. Out of the four species, *N. albicilla* acquired the highest heavy metal concentrations. Subsequently shells of *N. albicilla* collected from different sites around the Indian Ocean were compared for their metal concentrations. Shells of industrial sites in Kenya and India had significantly higher heavy metal concentrations than shells from pristine sites in Mauritius and Aldabra. Discussing the factors that may affect the shell metal concentration, the variations encountered herein are best attributed to the ambient bio-available metal concentration.

1. INTRODUCTION

In addition to their natural occurrence in the marine environment, heavy metals are introduced with industrial wastewater. Recently the world has witnessed an industrial boom in developing countries, where environmental quality standards are not well developed. This makes monitoring of heavy metals, especially in tropical and subtropical seas a pressing necessity.

Heavy metal pollution can be monitored in seawater, sediment and biota. Seawater provides a direct approach to detecting sources of metal pollution. However, the concentrations in seawater are usually low and pre-concentration is needed. Also metal concentrations in seawater depend on the water type and do not necessarily represent the metal toxicity. Therefore, comparison of metal concentrations in different water types is not meaningful. Sediment may help in identifying industrially affected areas and use of sediment cores may provide a historical record of the heavy metal burden. However, metal concentrations in sediment depend strongly on the analytical method. Also the concentration depends on many physical and chemical factors, such as sedimentation rate and organic carbon content. Besides, metal concentrations in sediments do not represent the metal bio-availability. Biota provides a direct measure of metal bio-availability and metals are usually accumulated (pre-concentrated) in some organisms, which makes the analysis relatively easy. However, not all organisms accumulate metals, and not all metal accumulating organisms can serve as bio-monitors, because some organisms are capable of maintaining a fixed body regulated heavy metal level, irrespect of the ambient concentration..

Traditionally, talking of biological indicators automatically meant talking of soft tissue. However, heavy metal concentrations in soft tissue depend on many Physiological, environmental and temporal factors. Also determining a soft tissue natural wet weight is a problem. Shells on the other hand have received much less attention than has soft tissue. However due to the numerous interactions with metal concentration in the soft tissue, shells have been suggested as a biological condition independent parameter of metal concentration [1-3] and thus more transparent in reflecting the ambient metal concentration. Also assessment of metals in shells has been reported by [4] to have many advantages over that in soft tissue; shells are more readily maintained for long periods before assay, both in the field and laboratory, they are easy to isolate cleanly from the whole organism and problems related to depuration of the animal before analysis are avoided, shells may serve as a geological record of man induced changes in metal levels in the environment [5] and the biological half life of metals in shells is much longer than that in soft tissue [6].

Neretidae species comprise a considerable fraction of the biomass of the rocky inter-tidal habitat, in the tropical and subtropical regions. They graze upon thin films of blue-green algae, diatoms and detritus covering rocks in the inter-tidal zone. Through feeding and producing copious quantities of faeces, composed largely of fine rock particles, rasped off by the radula, they contribute significantly to the biological reworking of coastal sediments [7], and consequently to the redistribution of metals in the rocky inter-tidal environment. They have a long life span of 3-4 years on average. Interestingly distinguished is the *N. albicilla* which has an average life span of 6 - 7 years and may live up to 12 years [7].

The aim of the study was to investigate the appropriateness of shells of the *Nerita* family to serve as biological indicators of heavy metal pollution in the tropical and subtropical waters. The main objectives of the study were (i) to assess the metal concentrations and the mineralogy of shells of different *Nerita* species (ii) to study the shell weight metal concentration relationship and (iii) to study the ability of the species that turns out to be distinguished in its metal concentrations, if any, to reflect the heavy metal environmental burden.

2. MATERIALS AND METHODS

2.1. Sampling sites

Shells were collected from five locations on the Indian Ocean (Fig. 1), Phuket Island, India, Kenya, Mauritius and Aldabra.

Phuket Island: The sample was collected from a rock - coral platform at the southern end of Patong Bay, off Thailand. The collection site extends in front of a hotel that discharges untreated sewage into the sea, through a 30m pipe, which ends at a water depth of about 0.5 m at low tide. The main human impacts on the Island are due to tourist activity, and the ongoing construction of new hotels.

India: A common feature of the Indian coast is the presence of many major river outlets and consequently a strong sedimentation regime. The sample was collected from Quilon, State of Kerala, on the south-western part of the Indian coast. Climate at the sampling site is typically tropical, where both south - west and the north - east monsoons contribute to a total annual rain fall of about 1600 mm. The main human impacts on the site are due to effluents of chemical industry and untreated sewage .

Kenya: The Kenyan continental shelf is narrow and supports fringing and patch reefs, which lie mostly 0.5-2.0 km offshore. Samples were collected from Bamburi Beach, just north of the port of Mombasa. The common current in the area is the Eastern African Coastal Current, which flows along the Kenya coast causing a northward water movement for most of the year. Heavy rains mainly in April and May cause large pulses in river derived sediments. The main human impacts on the sampling site come from the Athi drains, carrying effluents of the country's main industrial centre around Nairobi, and from the large industrial port of Mombasa.

Mauritius: Mauritius is a small island located off the east African coast in the West Indian Ocean and surrounded with about 150 km of fringing reef cut by surge channels and river mouths. Samples were collected from Le Morne, on the extreme south-west coast of the island, approximately 34 km south of the capital Port Louis. The Mauritian coast in general suffers from pesticide runoff from agricultural land, and from suspended solids accompanying sewage outfalls on parts of the west coast. However the samples were taken from a relatively clean site, proposed to become a marine park or a protected area.

Aldabra: Aldabra is a coral atoll located in the west Indian Ocean between the northern tip of Madagascar and Mombasa. Much of the coastline consists of deeply undercut limestone cliffs and a broad inter-tidal reef flat. The atoll boasts the largest land area in the Seychelles. Samples were collected from West Island, at the north-west of the atoll. The atoll is managed by four subcommittees under the Seychelles Island foundation, who maintain a policy of minimum human interference. As compared to the other sampling sites the sampling site here experiences negligible anthropogenic input.

2.2. Analytical methods

Around 20 individual shells were analysed for crystallography by X ray diffraction and for the concentrations of Mg, Sr, Mn, Fe and Zn by atomic absorption spectrophotometry. During sample collection damaged or heavily encrusted shells were rejected. Before analysis the shells were cleaned with dilute hydrochloric acid and hydrogen peroxide so that any metals adsorbed onto the periostracum are removed and only metals which are integral parts of the shell matrix would be assessed. Standards were prepared in solutions containing aliquot weights of $CaCO_3$ equivalent to those of the shell weight in the sample digests.

3. Results and discussion

3.1. Shell weight effect on the accumulation of metals

Metal concentration in the four Nerita species were plotted against shell weight and the plots showed no significant relationship between the concentration of any metal and the shell weight in any species. This was confirmed statistically by regression analysis, where no significant correlation coefficient was found between any metal concentration and the shell weight in any of the four species.

3.2. Comparison between metal concentrations in the four Nerita species

Average concentrations of Mg, Sr, Mn, Fe and Zn in shells of the four *Nerita* species are shown in Fig. 1. Statistical comparison of metal concentrations in the different species shells is summarised in Table 1.

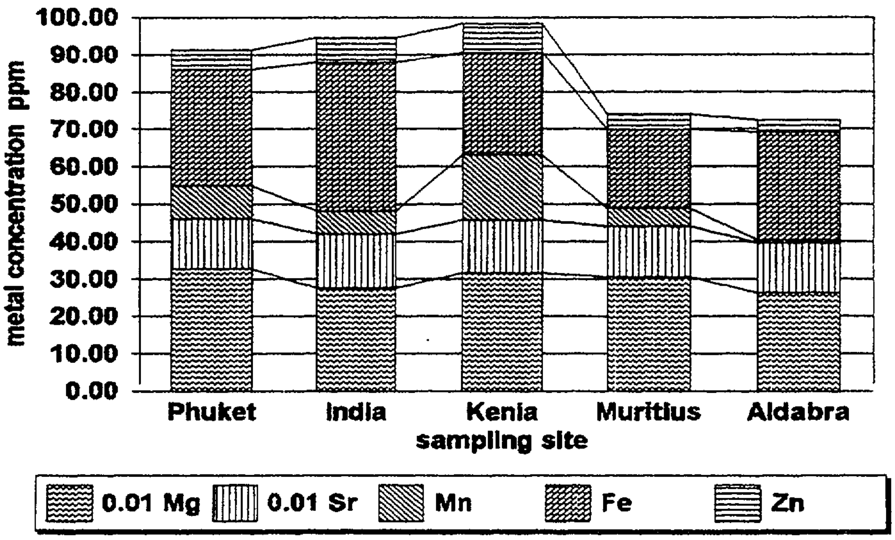

FIG 1. Comparison between metal concentrations (ppm) in shells of four Nerita species collected from Phuket Island, Thailand.

TABLE I. Statistical comparison amongst metal concentrations in the four Nerita species. Species are given ranks in ascending order with increasing heavy metal; (Zn, Fe, Mn) concentration. Metal concentration in all shells conformed to normal distribution and no application if paraneteruc statistics possible and thus ANOVA followed by pairwise multiple comparison was used. Non-significantly different species with respect to the metal rank of the shells of N. albicilla and the lowest rank of the shells N. polita. Shells of the other two species have intermediate and similar ranks.

Species	Zn	Fe	Mn	Sr	Mg	THR
N.albicilla	2	2	3	1	2	7
N.polita	1	1	1	2	1	3
N. costata	2	1	2	3	2	5
N. undata	2	2	1	1	2	5

THR= Total Heavy Rank.

3.3. What is different about *albicilla* shells?

3.3.1. Crystallography?

The distribution of magnesium and strontium in shells of ninety five molluscan species, which are either wholly aragonite or calcite [8] shows that calcitic shells have a magnesium concentration of about ten fold that of the aragonite shells, with no overlap in the concentration range, but with some exceptions. Strontium concentration, on the other hand, could be similar in the two crystal types, but with a tendency of being higher in aragonite shells. Gastropod shells of the present study seem to be amongst the exceptions with respect to magnesium. They have a high aragonite fraction (Fig. 2), but the magnesium concentrations (Figs. 1; 3) are typical of those of purely calcite shells.

The metallic characteristics of calcium carbonate crystals might be explained on the basis of easier substitution of the relatively small magnesium ion for the larger calcium ion in the calcite lattice, which is isostructural with magnesite ($MgCO_3$). Most trace metals also have smaller radii than calcium and would be expected to substitute for calcium more easily in calcitic crystals. In contrast, strontium which has a larger radius than calcium can be incorporated more easily in aragonite which is isostructural with strontianite ($SrCO_3$) However, the ionic radii argument is somewhat controversial, because metals in solution interact as hydrated ions and the hydrated ionic radii are inversely proportional to their corresponding metallic radii [9].

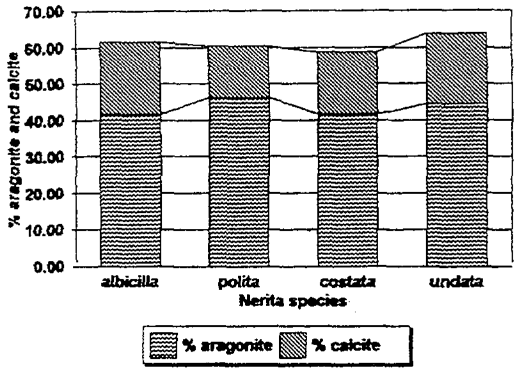

FIG 2. Average % aragonite and % calcite four Nerita species from Phuket Island

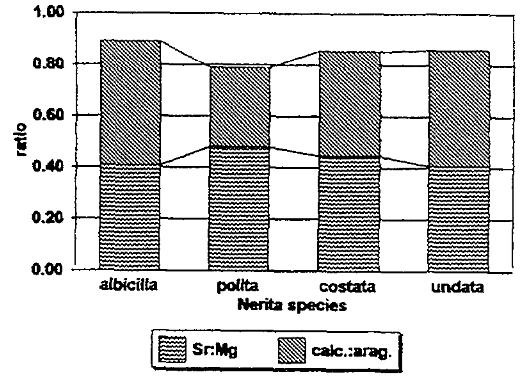

FIG 3. Average Sr-Mg and calcitearagonite in the ratios in the four Nerita species from Phuket Island

Within the four species studied herein, there is a good agreement between the concentrations of magnesium and strontium on one side and the shell crystallography on the other. Shells of *N. albicilla and N. undata* which have similar high mean concentrations of magnesium and low mean concentration of strontium, have the highest mean calcite - aragonite ratio. Shells of *N. polita* which are significantly lower than the others in their magnesium concentration have the lowest mean calcite - aragonite ratio. Furthermore, a significant negative correlation coefficient exists between strontium - magnesium ratio and the calcite - aragonite ratio in all the samples analysed irrespective of the species. However, the agreement between shell crystallography and the minor metals does not seem to explain much of the trends in trace metal concentrations. Although almost identical in crystallography as well as in magnesium and strontium concentration, shells of *N. albicilla and N. undata* are very different in their manganese concentration. Noteworthy is that manganese replaces calcium in calcite and aragonite crystals indiscriminately [10]. According to [8], considering other factors affecting the distribution of minor and trace metals in shells, it is not surprising that the correlation with crystal type is not especially strong.

3.3.2. What else?

The shell growth rate has been reported as a major factor controlling its metal concentration According to [11] the faster the growth rate of the shell the less the concentration of magnesium and manganese, and the higher the concentration of strontium. Growth rate in turn might be affected by zonation. The lower the animal is with respect to the shore line then the longer the submergence time, the greater the food availability through filtration and the faster the growth rate. *Nerita* species are well known for their distinct zonation patterns. *N. albicilla* is a low shore species and may exist sub-tidally and *N. polita* is an upper shore species. However, *N. albicilla* is the slowest growing and *N. polita* is fast growing. Consequently, the zonation theory fails to explain the metal concentration patterns in the Nerita species. Noteworthy is that the *Nerita* species are not stationary feeders but move around mainly during night to collect their food [7] and that *N. albicilla* has a much longer life span than all the other species. This may suggest genetic differences to account for the difference in growth rate and consequently for the significantly higher metal concentrations in the shells of *N. albicilla.*

3.4. Comparison between metal concentrations of *N. albicilla* shells from different sites on the Indian Ocean

Having found that shells of *N. albicilla* acquire relatively high heavy metal concentrations, we raised the question whether these concentrations were species specific or environmentally related. Metal concentrations in *albicilla* shells collected from five different sites around the Indian Ocean (see materials and methods) were compared. Results of the comparison are summarised in Fig. 4. and Table II.

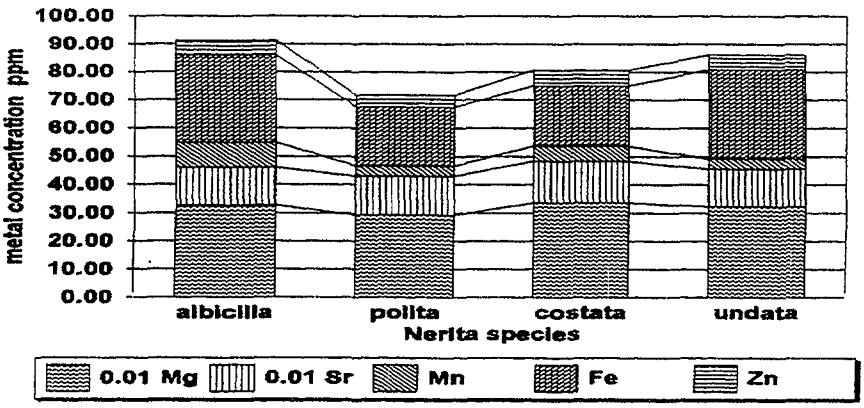

FIG.4. Comparison between metal concentrations (ppm) in shells of N. albicilla from different sites on the Indian Ocean

TABLE II Statistical comparison amongst metal concentration in shells of N. albicilla from different sites around the Indian Ocean. Sites are given ranks in ascending order with increasing heavy metal; (Zn, Fe, Mn) concentration. Metal concentration in all shells conformed to normal distribution and no metal concentration-weight interaction existed in the shells from any site. This made the application of parameteric statistics possible and thus ANOVA followed by pairwise multiple comparison was used. Non significantly different sites with respect to the concentration of a specific metal were given the same rank. Clear is the highest heavy metal rank of the shells from Kenya and the lowest rank of the shels from Aldabra. .

Site	Zn	Fe	Mn	Sr	Mg	THR
India	4	4	2	2	1	10
Kenya	5	2	4	2	2	11
Aldabra	1	2	1	1	1	4
Mauritius	2	1	2	1	2	5
Phuket	3	3	3	1	2	9

THR=Total Heavy Rank

The lowest heavy metal concentrations were found in the shells from Aldabra, a natural reserve relatively pristine site, and the highest concentrations in the shells from Kenya and India, sites that suffer from industrial inputs (see materials and methods).

3.5. Effect of environmental factors

The effect of environmental factors on heavy metal concentrations in shells of marine animals has been considered by several authors. [12] ruled out the effect of temperature and salinity on the accumulation of manganese in shells of two species of barnacles and attributed higher manganese concentration to higher total metal concentration in the local environment. This is because manganese can be directly incorporated into the shell, as manganese oxide, through mineralization both in the soluble and colloidal phases. [11] studying the structural and environmental controls of trace metals in shells of five species of barnacles, also reached a similar conclusion. According to [11] the uptake of the metal is faster when and where the ambient concentration is higher. A similar argument has also been put forward by [13] regarding iron.

The environmental concentration of zinc has also been suggested to affect the metal concentration in the shell [6] mainly by inhibiting the carbonic anhydrase activity, which affects the rate of calcium deposition for the benefit of deposition of other metals, including zinc itself. [14] reported that high concentrations of at least the metals manganese, copper and zinc in the oyster shell are due to relatively high concentrations of these metals in the seawater.

[15] reported a preferential accumulation of environmentally available manganese, cobalt, and lead in the shells of *Villorita cyprinoides* rather than in the soft tissue
Hence, in context of the above discussion and the environmental conditions prevailing at the sampling sites, the variations in manganese, iron and zinc concentrations in the shells of *N. albicilla* from the different sites are best explained by variations in bio-availability of the metals in the sea water and reflect the heavy metal environmental stress.

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EFFECTS OF NUCLEAR AND NON-NUCLEAR POLLUTANTS ON MARINE ECOSYSTEMS

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Abstract

Effects of nuclear and non-nuclear pollutants on the Black Sea marine ecosystems are reviewed with special emphasis on the work which has been carried out in the IBSS.

1. INTRODUCTION

Radioecological research at the Black Sea, initiated in 1956 at the A.O.Kovalevsky Sevastopol Biological Station, reorganised later into the IBSS, National Academy of Sciences of Ukraine, includes two main aspects: a) biogeochemical migration of radionuclides and other major pollutants [1-3] as well as b) biological effects of ionising radiation and chemical pollutants [1, 4, 5]. Levels and transfer of radionuclides in the Black Sea, mostly in its NW part, are studied at the IBSS (in the framework of IAEA TC RER/2/003, EC contracts) and by other institutions [6-10].

It is of a principal interest to try to compare ecological effects of ionising radiation and chemical pollution in the marine environment upon the Black Sea wildlife in equivalent doses.

2. MATERIAL AND METHODS

This paper is an attempt to combine the following approaches together:

- Existing wild natural ecosystems' observations at IBSS, Sevastopol/Odessa, and at the other biological institutions during a very long period – decades of years (changes of biological components in ecosystems and of anthropogenic stresses in the environment) in the Black Sea [7, 11];
- Published data of studies with the help of aquatic microcosms - controlled ecosystems at the National Institute of Radiological Sciences, Japan (on the basis of quantitative measurements of the ecosystem dynamics depending on doses of deleterious factors) [12, 13] and
- Proposed by the author [5], the radiochemoecological conceptual model of effects in all possible scale of deleterious factors.

As for the present work, dose rates of ionising radiation and doses of chemical pollutants in the Black Sea environment to aquatic plants and animals were assessed on the base of the available data of the IBSS and other works (devoted to nuclear/non-nuclear sources in the environment of this sea) [2, 3, 6-10, 13-15].

The author had proposed [16] and later developed [4] a conceptual model of responses of organisms, populations and ecosystems to all possible dose rates of ionising radiation in the environment (with the following zones of radiation effects: radiation well-being; physiological masking; ecological masking; and damage to ecosystems zones). Recently, this model was extended and transformed by the author into a radiochemoecological model, which covers not only ionising radiation effects but also chemical pollutants action [5].

3. RESULTS AND DISCUSSIONS

Fig. 1 represents general radiochemoecological conceptual model of zones of ecological impact by chronic ionising irradiation [5] with the special indication of ecological deleterious consequences in the Black Sea ecosystems, using the following ecological criteria:

- Decrease of number or total mass (of populations),
- Decrease of number of species (of communities) and
- Degradation of communities (of ecosystems).

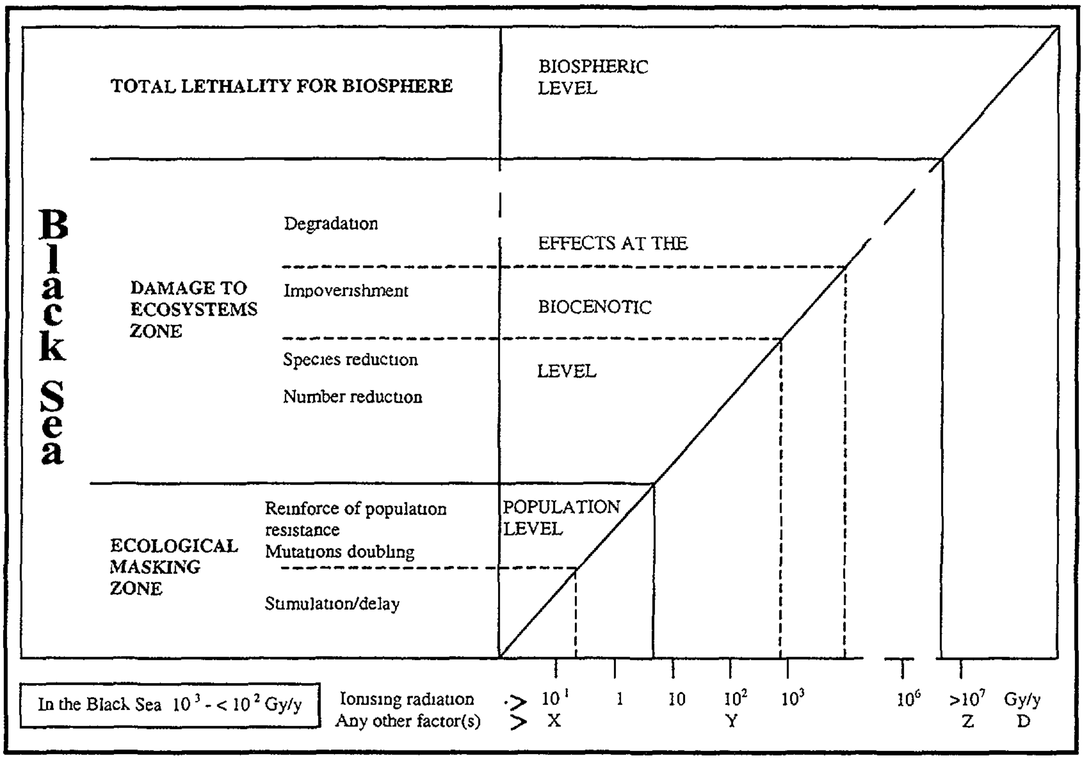

FIG. 1. Long-term dependence of populations/ecosystems reactions on ionising radiation dose rate as well as any chemical or physical factors dose in 'masking' and 'damage' zones. X, Y, Z - conditional quantities of doses D of non-radioactive factors [5]. The Black Sea marked ecological impact is connected to non-nuclear factors because of lack of higher ionising radiation doses.

It is obvious that dose commitments of environmental ionising radiation to the Black Sea organisms are in the 'Well-Being Zone' however chemical pollutions, including, first of all, eutrophiers a.s.o., produce directly and indirectly severe ecological effects, which are identical in manifestation to action under higher and very high dose rates of ionising radiation, available only in very few nuclear areas, such as MAYAK, Chelyabinsk Region. Chemical pollutions in the estuarian and shelf areas of the Black Sea cause heavy ecological effects, typical for the 'Damage to Ecosystems Zone' (Number reduction, Species reduction, Impoverishment, Degradation) under the action of chemical chronically-acting doses, which are obviously equivalent to the orders of, and higher than, 20 to >1000 Gy/y of ionising radiation dose rates.

Fig. 2 demonstrates a good agreement of the microcosm data by S. Fuma et al. on nuclear/non-nuclear impacts [12] and the radiochemoecological conceptual model by Polikarpov [5].

Available measurements of metals (e.g., Cu) in the bottom sediments (1.75 to 6.17 mg/kg) and in mussels (3.62 to 6.89 mg/kg) of the Kerch Straight [17] show that, taking into account rather significant concentration factors of Cu in hydrobionts, the content of this metal in the environment (28 to 97 μmol/kg) and in the mussels bodies (57 to 108 μmol/kg) is, perhaps, a few orders of magnitudes lower in the Black Sea than the level of its severe ecological influence on the microcosm, registered by S. Fuma et al. [12].

Fig. 3 is a map of pollution sources at the Black Sea [7].

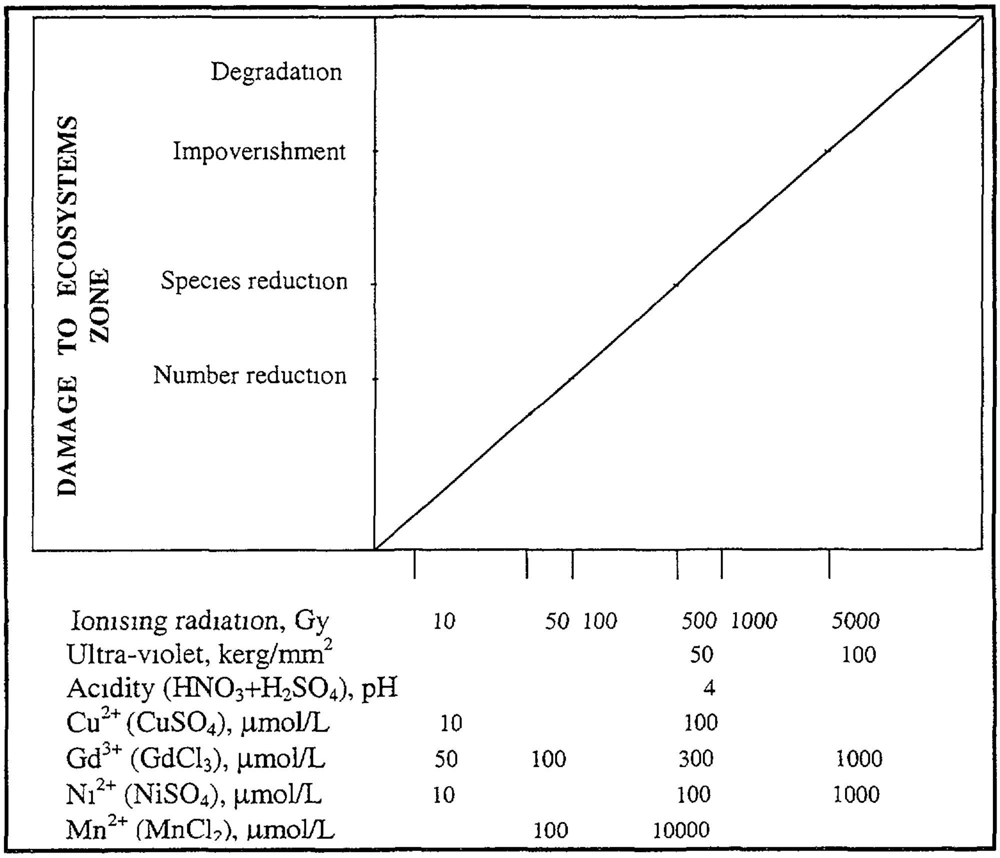

FIG 2 Radiochemoecological model [5] combined with data on toxicants' ecological effects in the aquatic microcosm [12]

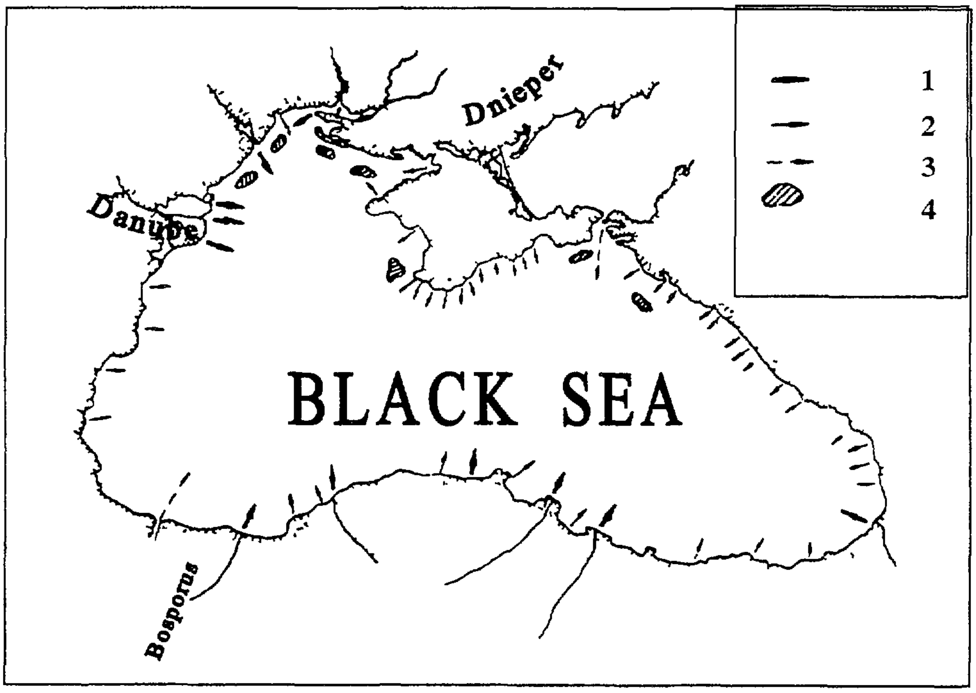

FIG 3. Scheme of location of large-scale sources of the Black Sea pollution [7]
1 – sewage waters input with river flows;
2 – direct discharges of sewage waters through sewage outlets;
3 – polluted waters input from adjacent seas,
4 – dumping

TABLE I. DAMAGE TO ECOSYSTEMS AND POPULATIONS OF THE BLACK SEA SPECIES CAUSED BY NUCLEAR AND NON-NUCLEAR POLLUTIONS

Ecological damage assessments [11]	Lethal Chronic Doses of Ionising Radiation (Gy) [19]	Equivalent Lethal Chronic Doses of Non-Nuclear Pollutions (Gy-eq./y) A	Environmental Nuclear Sources, (Gy/y) B [2, 7, 15]	Ratio A/B
1. ***Cystoseira barbata* biocenosis.** > 99 % of its population size were lost since 1960s on Romanian & Ukrainian shelf under eutrothication & pollution impact	For *Thallophyta* (including algae) 180-72000	180-72000	< 0.005	10^4-10^7
2. **Gen. *Phyllophora* biocenosis.** 97 % of population size were lost during 30 years on NW Black Sea under press of eutrophication, pollution & turbidity	For *Thallophyta* (including algae) 180-72000	180-72000	< 0.005	10^4-10^7
3. ***Ostrea edulis*.** > 95 % of its population were lost during 30 years on the Black Sea shelf under turbidity action	For *Mollusca* 600-6000	600-6000	< 0.007	10^5-10^6
4. ***Mytilus galloprovincialis*.** 60 % of its population were lost during 30 years on the Black Sea shelf under action of hypoxia, caused by eutrothication	For *Mollusca* 600-6000	600-6000	< 0.007	10^5-10^6
5. ***Crustacea* populations.** Crabs (14 species) & shrimps (> 20 species) were lost 50-70 & 60 % of their populations during 30 years under action of overharvesting of crabs & hypoxia for shrimps	For *Crustacea* 90-3600	90-3600	< 0.007	10^4-10^5
6. ***Gobiidae* populations.** All 20 species were lost 80 % of their populations on the shelf during 30 years under action of hypoxia on the bottom & destruction of their breeding grounds	For *Pisces* 42-360	42-360	< 0.007	10^4-10^6
7. **Marine *Mammalia* populations.** Dolphins (3 species, endemic subspecies) lost 90-95 % of their populations sizes during 30 years as consequences of toxicants biomagnification & killing as bycatch in fisheries. Number of monk seal (*Monachus monachus*) decreased to few individuals (or to 0) because of lack of reproduction on coastal areas & toxicants biomagnification	For *Mammalia* 12-90	12-90	< 0.006	10^3-10^4

The distribution of differently polluted water along sea-shore of Ukraine, Russia and Georgia was studied [18].

The results of the paper describe the state of dominant and former dominant species of the Black Sea plants and animals, including some of them, now disappeared from the stage of life. Assessments of equivalency of real existing non-nuclear pollutants' after-effects in the Black Sea ecosystems are proposed to express in the units of ionising radiation equivalent dose rates, Gy-eq./y.

The proper data on the influence upon the Black Sea ecosystems, communities and populations as well as ratios of the assessed equivalent dose rates by non-nuclear pollutants to the existing dose rates of ionising radiation in the ecosystems are presented in Table 1. According to [19], the chronic lethal dose is 2 to 10 times higher than the acute lethal dose. Their mean ratio, equalled to 6, is accepted for this paper.

4. SUMMARY

Severe chronic and acute effects, produced by non-nuclear pollutants on the Black Sea shelf and estuarian ecosystems, are quantitatively equivalent to the ecological effects of nuclear pollutants/contaminants in the Chernobyl NPP' nearest (few km) zone, the Kyshtym trail, the Karachay Lake and other similar specific nuclear areas in the World. This situation at the Black Sea needs cardinal amelioration both on the basis of wild-life protection [20] and on the principals of eco-ethics [21]

There is a great lack of knowledge on quantitative ecological effects of hydrogen sulphide, deficiency of oxygen and many other non-nuclear factors.

Both the proper monitoring in nature [5, 22] and use of a microcosm [12, 13] are needed.

It is proposed to develop for the future, if possible, under the IAEA aegis: a detailed substantiation of equivalency approach in comparing of nuclear and non-nuclear pollutants' ecological impact as well as creation of comparative molismological theory of ecological equivalency of effective doses of all kinds of ecologically-deleterious significant sources (electromagnetic, mechanical, chemical), including lack or excess of vitally important substances. It is a big, but unavoidable work in the field of ecological radiochemoprotection.

Radioecology of potentially high dose rate, effective for natural ecosystems, will be permanently necessary at the age of nuclear energy with its potential nuclear accidents and even non-excluded nuclear terrorism.

Environmental radioactivity is an excellent and a very sensitive ecological tool for studies of nuclear and non-nuclear pollutants: a/ ecological effects as well as b/ their fate in the sea, including their pathways up to a man.

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RIVERINE TRANSPORT OF Cs-137 AND Sr-90 INTO THE BLACK SEA AFTER CHERNOBYL ACCIDENT (DATA ANALYSIS AND METHODOLOGICAL ASPECTS OF MONITORING)

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Abstract

Upper part of Dnieper catchment had been heavily contaminated after the Chernobyl accident and serves as a main source of the secondary input of radionuclides to the river. As a result of fast sorption of dissolved radiocesium by suspended sediments and sedimentation of contaminated particles to the bottom, practically all the ^{137}Cs having entered into the upper reaches of the Dnieper river after the Chernobyl accident was retained in the Dnieper reservoirs and the Dnieper-Bug estuary. Taking into account relatively high mobility of ^{90}Sr the extent of it's trapping by Dnieper reservoirs is significantly less comparatively to ^{137}Cs and accounted as some 60-70%.

The Danube River catchment is characterized by less radioactive contamination, in comparison with the Dnieper catchment, and more homogeneous spatial distribution of this contamination. Suspended particles play a crucial role in ^{137}Cs transport by Danube to the Black Sea. Regular observations showed, that in average 60-70% of ^{137}Cs transport to the Black Sea is associated with suspended particles. The conditions for water selfpurification are absent on the Danube River due to the high velocity of the currents along the whole it length. Therefore, the significant portion of ^{137}Cs and other contaminants in particulate phase washed out from the upper part of basin can reach the Black Sea.

The correct accounting of ^{137}Cs discharge on suspended particles by river strictly depends on representativity of samples used in calculation. Sampling procedure which had been done in uncorrect way could cause in significant underestimation of ^{137}Cs concentration up to 10 times.

1. INTRODUCTION

River's flow is a second of other sources by its contribution on the Black Sea radioactive contamination [1]. The volume of the Dnieper and Danube runoff accounts for 75% of the total river runoff in the Black Sea [2]. The catchments of these two rivers were affected by the Chernobyl contamination at the most extent [1]. The contribution of other rivers to the radioactive contamination of the Black Sea was not studied, but it is assumed that this value is not significant [3]. So, for example, Caucasus coast river runoff had relatively considerable effect on the formation of the surface concentration field on the adjacent sea area in the spring 1987 only [4].

The Ukrainian Hydrometeorological Service began to conduct the regular observations on the ^{137}Cs content in the water of Lower Danube from the September 1997. Earlier, the main efforts in observations were concentrated on the Dnieper River and its tributaries, which flows through the mostly contaminated in consequence of the Chernobyl accident territories.

The evaluation of the Danube and Dnieper rivers role in the Black Sea radioactive contamination after Chernobyl accident had been carried out by the different investigators. The review and generalisation of the results of these investigations is carried out in Ref. [1].

The observations conducting on the Danube River from the September 1997 allowed to extend our insights about the distinctions of radionuclides transport in these two rivers systems. The accounting of these distinctions is important for the correct choice of the methodology of observations.

2.1 Dnieper River

Upper part of Dnieper catchment had been heavily contaminated after the Chernobyl accident and serves as a main source of the secondary input of radionuclides to the river. The reservoirs which were built on the Dnieper (Dnieper cascade) are immense sedimentational traps. The retarded flow (up to a year) of water masses from the upper reaches of the river to the mouth, through the body of cascade, creates the ideal conditions for accumulation of radionuclides and other contaminants in all the components of reservoirs ecosystem.

The general scheme of selfpurification of Dnieper River from ^{137}Cs and some others radionuclides is as follows: initial entering to the water column of clean suspended material derived both by reservoir's shoreline abrasion and side-rivers output, followed by fast sorption of dissolved radiocesium onto this material and sedimentation of contaminated particles to the bottom. As a result of this process, practically all the ^{137}Cs having entered into the upper reaches of the Dnieper river after the Chernobyl accident was retained in the Dnieper reservoirs and the Dnieper-Bug estuary. Taking into account relatively high mobility of ^{90}Sr the extent of it's trapping by Dnieper reservoirs is significantly less comparatively to ^{137}Cs and accounted as some 60-70%. Another important process, responsible for the irretrievable sinking of ^{90}Sr from water column to the bottom, apart of sedimentation, is including of radionuclide to the chemical structure of mollusc shells during its growth.

At present the concentration of ^{137}Cs in water of the Lower Dnieper came back to the pre-Chernobyl level while concentration of ^{90}Sr exceeds one in 4-5 times. More than 90% of ^{137}Cs and almost all ^{90}Sr are transported to the Dnieper-Bug Estuary and further to the Black Sea as a dissolved fraction.

The ^{137}Cs concentrations in the Lower Dnieper during 1997-1998 (Fig.1) has been changed in the range of 0.13-1.5 Bq/m^3 (the mean value is 0.53±0.24 Bq/m^3) and it were in two order lower, than in the upper part of the Dnieper River system. The range of ^{90}Sr concentration changes is 26-126 Bq/m^3 (the average is 77.9±40.0 Bq/m^3). The peak of ^{90}Sr concentrations in February of 1998 is plainly manifested. This peak is caused by the ingress of contaminated water mass, which was formed in the Chernobyl zone during the spring flood of 1997.

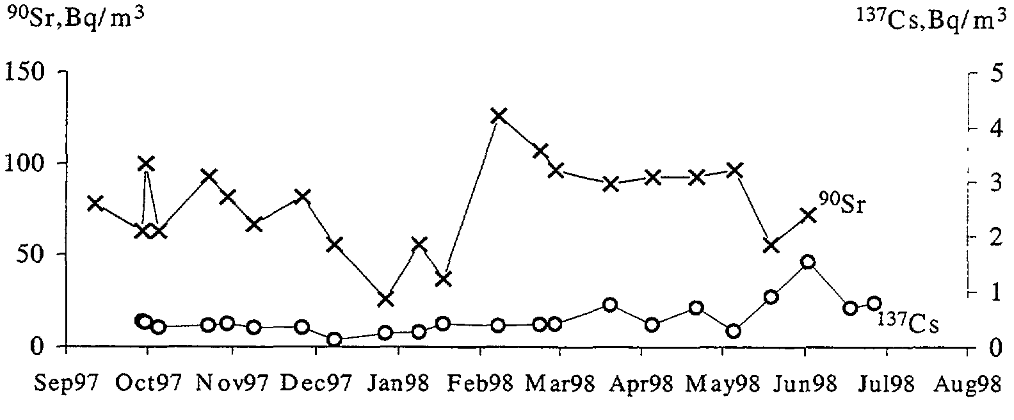

FIG 1. Concentrations of ^{137}Cs and ^{90}Sr in Dnieper surface water collected near Nova Kakhovka during September 1997 - June 1998.

TABLE I. Estimated Values of ^{137}cs and ^{90}sr Inlet to the Black Sea (Dnieper-Bug Estuary) within the Dnieper River Flow, September 1997 - June 1998

Period	**Dnieper runoff, km^3**	**^{137}Cs**		**^{90}Sr**	
		Bq/m^3	**GBq**	**Bq/m^3**	**GBq**
Sept 1997	4.137	0.46±0.07	1.90	70.4±14.8	291.2
Oct 1997	5.108	0.40±0.08	2.04	84.3±22.6	430.6
Nov 1997	5.135	0.35±0.05	1.80	74.1±14.8	380.5
Dec 1997	4.363	0.19±0.06	0.83	40.8±14.9	178.0
Jan 1998	2.328	0.34±0.08	0.79	46.3±18.6	107.8
Feb 1998	3.172	0.39±0.06	1.24	117±20.0	371.1
Mar 1998	4.928	0.59±0.17	2.91	92.6±22.2	456.3
Apr 1998	7.120	0.56±0.15	3.99	92.6±19.2	659.3
May 1998	7.599	0.60±0.30	4.56	76.0±30.4	577.5
June 1998	5.796	1.12±0.42	6.49	72.0±14.6	417.3
Sept 1997 - June 1998	49.686		26.55		3870.0

The ^{137}Cs concentrations in the Lower Dnieper during 1997-1998 has been changed in the range of 0.13-1.5 Bq/m^3 (the mean value is 0.53±0.24 Bq/m^3) and it were in two order lower, than in the upper reaches of the river. The concentrations of ^{137}Cs transported by the suspended sediments has been changed in the range of 0.03-0.13 Bq/m^3 in 1997-1998. The mean value is 0.05±0.03 Bq/m^3 (less than 10% from the total content) under the turbidity changes in the range 0.3-2.8 g/m^3.

During September 1997 - June 1998 the 0.027 TBq of ^{137}Cs and 3.87 TBq of ^{90}Sr were carried out by the Dnieper River to the Dnieper-Bug estuary (Table 1).

2.2 Danube River

The Danube River catchment is characterized by less radioactive contamination, in comparison with the Dnieper catchment, and more homogeneous spatial distribution of this contamination [5].

The water runoff of the Danube River in contrast of the Dnieper River is not regulated. It was shown above that the sedimentation of the solid material plays a significant role in decreasing of radionuclides concentration in water. The conditions for water selfpurification are absent on the Danube River due to the high velocity of the currents along the whole it length. Therefore, the significant portion of ^{137}Cs and other contaminants in particulate phase washed out from the upper part of basin can reach the Black Sea.

Specific feature of the Danube River is the high content of suspended sediments in water (22-610 g/m^3 in 1997-1998), which play a crucial role in ^{137}Cs transport by this river to the Black Sea. The observations in location of Izmail are show, that 60-70% of ^{137}Cs is transported to the Black Sea by the suspended sediments. The close correlation are revealed between the content of the suspended sediments in the sample (g/m^3) and the volume concentration of ^{137}Cs (Bq/m^3) in suspension (Fig. 2, Table 2).

The most low total concentrations of ^{137}Cs (0.5 Bq/m^3) has been observed in September-November 1997 during low-water period with insignificant discharge of suspended particles. In contrary, at high-water period concentration of ^{137}Cs in river's water get increased in several times mostly due to increasing of suspended particles discharge. The specific content of ^{137}Cs in the suspended sediments during 1997-1998 has been changed slightly - from 14 to 36 Bq/kg (in average 24.4±10.0 Bq/kg). More than 90% of transported by the suspension ^{137}Cs is associated with fine particles less than 0.05mm, which apparently belong to transit fraction (Fig. 3, 4).

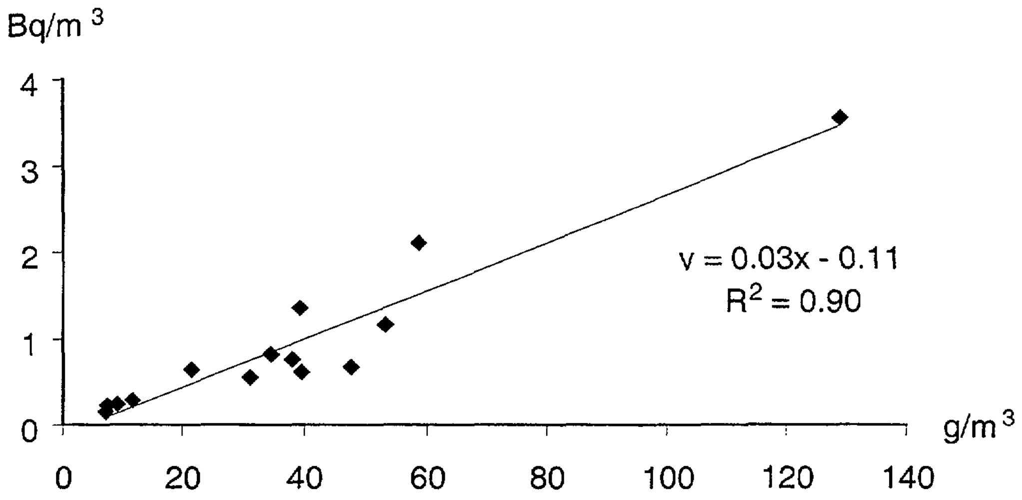

FIG. 2. The Connection Between Concentration of ^{137}Cs (Bq/m^3) in Suspension and the Content of the Suspended Sediments in the Sample (g/m^3).

TABLE II. Corellation Matrix with the Values of the Main Hydrological Characteristics and RadionuclideConcentrations in Crossection Danube-Izmail, September 1997 - July 1998

Parameter	T	Q	$^{137}Cs_{sol}$	$^{137}Cs_{sus}$	$^{137}Cs_{sum}$	Turb	U_{sus}	^{90}Sr
T	1							
Q	0.01	1						
$^{137}Cs_{sol}$	0.05	0.18	1					
$^{137}Cs_{sus}$	0.50	0.53	-0.06	1				
$^{137}Cs_{sum}$	0.60	0.50	0.21	0.95	1			
Turb	0.79	0.57	0.12	0.95	0.96	1		
U_{sus}	0.17	-0.03	-0.51	0.38	0.20	0.08	1	
^{90}Sr	-0.04	0.42	0.30	0.24	0.34	0.45	-0.50	1

Where: T - content of suspended sediments in river water (riverside);
Q - water discharge;
Turb - content of suspended sediments in the sample of water collected for radionuclide analysis;
U_{sus} - specific activity of suspended sediments

The values of the Danube River water and solid runoff during 1997-1998 were closed to its normal annual values. The dissolved ^{137}Cs concentrations in the Lower Danube at the same period has been changed in the range of 0.26-0.76 Bq/m^3 (Fig. 5) and it not revealed the dependence from the value of water discharge (Table 2).

So narrow range of the dissolved ^{137}Cs concentration fluctuations can be explained, from one side, by the uniformity of contamination of the Danube catchment, from another hand - by absence of significant changes in the water discharges during that period. For comparison: in 1997-1998 on the Prypyat River near Chernobyl the difference between minimal and maximal concentrations of the dissolved ^{137}Cs has reached 5.5 times.

During September 1997 - July 1998 the 0.3 TBq of ^{137}Cs and 9.8 TBq of ^{90}Sr were carried out by the Dnieper and Danube rivers to the Black Sea (Tables 1).

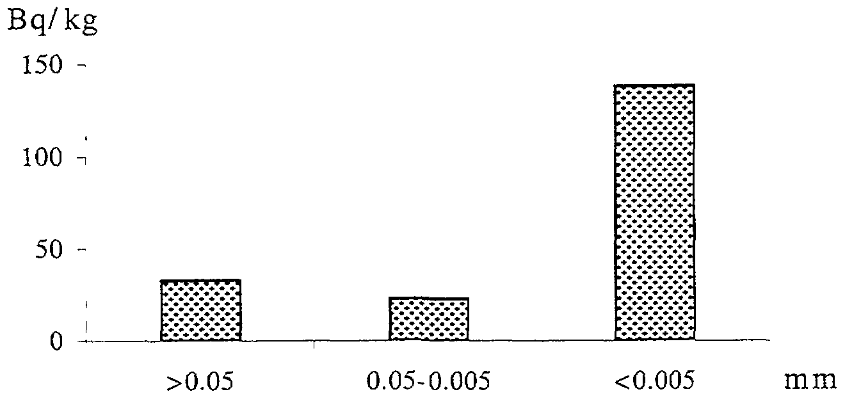

FIG 3. Distribution of ^{137}Cs over the size fractions of the Danube river suspended sediments, Danube-Izmail, 23 July 1998.

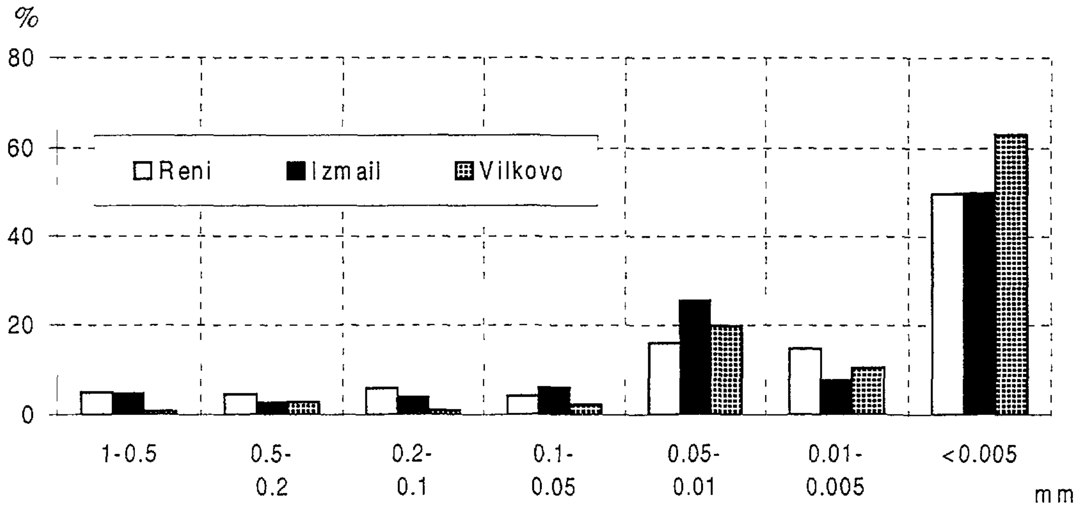

FIG 4. Granulometrical composition of the suspended sediments of the Danube River in 1997.

The analysis of the numerous monitoring data, carried out in the frames of IAEA Research Contract No. 7330/R2/RB "The Application of Tracer Techniques in Study of Processes and Pollution in the Black Sea" (1993-1995), allows to make the some conclusions about the Dnieper and Danube rivers role in radioactive contamination of the Black Sea after the Chernobyl accident.

1. During the whole post-accidental period the concentrations of ^{137}Cs in rivers water were significantly lower than in the surface layer of the Black Sea.

2. From 1987 up to now the concentrations of ^{90}Sr in rivers water are more higher than in the surface layer of the Black Sea.

3. During whole post-accidental period the concentrations of ^{137}Cs and ^{90}Sr in the Danube River water were lower than in the Dnieper. But runoff of the Danube river is in 4-5 times more than the Dnieper runoff, that promote a higher outflow of ^{137}Cs and ^{90}Sr in total comparable to that of the Dnieper River into the Black Sea.

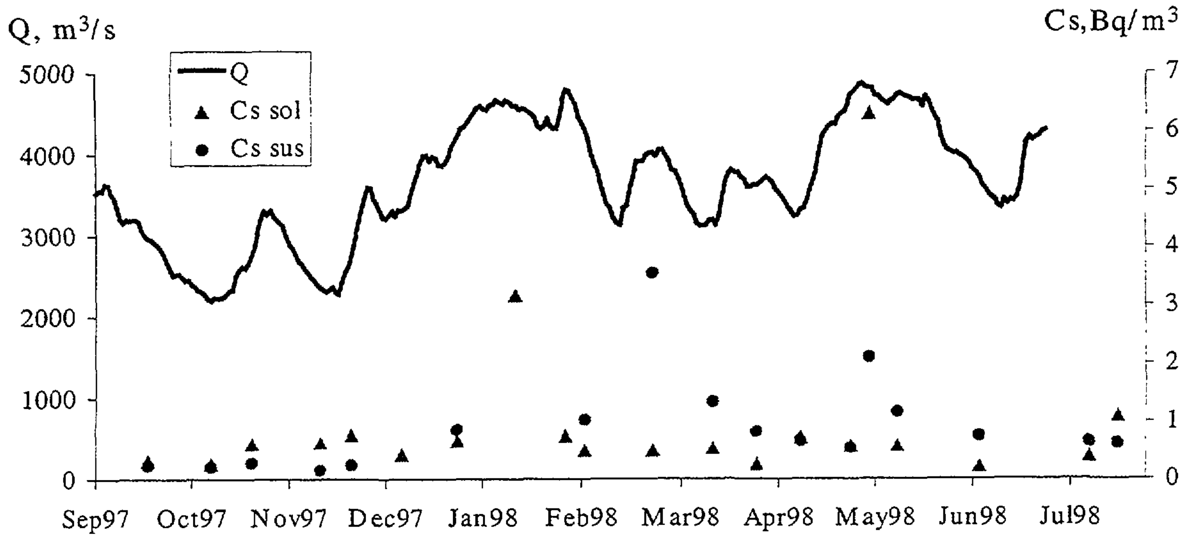

FIG 5. Concentrations of ^{137}Cs in Danube surface water collected near Izmail during September 1997 - July 1998.

TABLE III. Estimated Values Of ^{137}cs and ^{90}sr Inlet to the Black Sea within the Danube River flow, September 1997 - July 1998

Period		**Danube runoff, km^3**	**^{137}Cs, Bq/m^3**		**^{90}Sr, Bq/m^3**	**^{137}Cs, GBq**		**^{90}Sr, GBq**
			solut.	**susp.**		**solut.**	**susp.**	
Sept	1997	13.116	0.32±0.05	0.24±0.05	18.5±4.6	4.20	3.15	242.6
Oct	1997	11.812	0.44±0.18	0.25±0.06	11.1±3.7	5.20	2.95	131.1
Nov	1997	11.949	0.70±0.06	0.20±0.08	20.4±4.1	8.36	2.39	243.8
Dec	1997	17.410	0.54±0.12	0.85±0.18	27.8±5.6	9.40	14.80	484.0
Jan	1998	20.811	0.74±0.18	1.57±0.31	33.3±6.0	15.40	32.67	693.0
Feb	1998	15.580	0.49±0.08	2.29±1.10	24.1±5.5	7.63	35.68	375.0
Mar	1998	15.883	0.39±0.14	1.08±0.26	42.6±5.6	6.19	17.15	676.6
Apr	1998	17.211	0.64±0.10	0.60±0.06	48.2±14.9	11.02	10.33	829.6
May	1998	21.052	0.57±0.05	1.63±0.47	39.9±15.5	12.00	34.31	840.0
June	1998	16.667	0.21±0.03	0.75±0.21	33.3±7.0	3.50	12.50	555.0
July	1998	19.049	0.74±0.26	0.63±0.11	43.3±7.3	14.09	12.00	824.8
IX.1997	**-X.1998**	**180.54**				**96.99**	**177.93**	**5896**

4. The rivers has not an appreciable effect on the Black Sea contamination by ^{137}Cs, the value of it river transport remaines uncomparable lower, than it ingress on the sea surface from the atmosphere (at present 0.2-0.3 TBq/year).

5. About 120-140 TBq of ^{90}Sr have been carried out by Dnieper and Danube into the Black Sea during 1986-1998. The river derived share of ^{90}Sr input reached 23-25% of its total input from the different sources for the 12 years passed since the accident, and it continues to grow.

2. METHODOLOGICAL ASPECTS OF MONITORING

The significant uncertainties appears during the quality analysis of the data on radionuclides concentration presented by the different laboratories. The reason is in the different methodological approaches to the study of radioactive contamination of rivers. Most of researchers in their studies determined the total concentration of ^{137}Cs in water without it separation on soluble and particulate phases [6, 7, 8 and 9].

Meanwhile, without such separation it is impossible to unmask the reasons of the considerable temporal fluctuations of ^{137}Cs concentrations, as well as to assess the truth of adducing data (using, for instance, the typical values of watershed wash out coefficients for soluble ^{137}Cs). Besides, it is extremely important for such rivers as the Danube to provide analysis of the radionuclides flux to the sea and its further fate at the coastal area, separating the radionuclides transport for its dissolved and particulate phases.

The correct accounting of ^{137}Cs discharge on suspended particles by river strictly depends on representativity of samples used in calculation. The hydrological practice demonstrates that the suspended sediments are distributed in crossection of the river flow inhomogeneously: usually the decreasing of the suspended sediments concentrations from the bottom to the water surface, as well as from the middle of the river to the bank is observes. It means, that the sampling of water sample from the surface and near the bank can be caused in the considerable (up to order of magnitude) underestimation of riverine transport of the suspended sediments and radionuclides, which are associated with these sediments (Fig. 6).

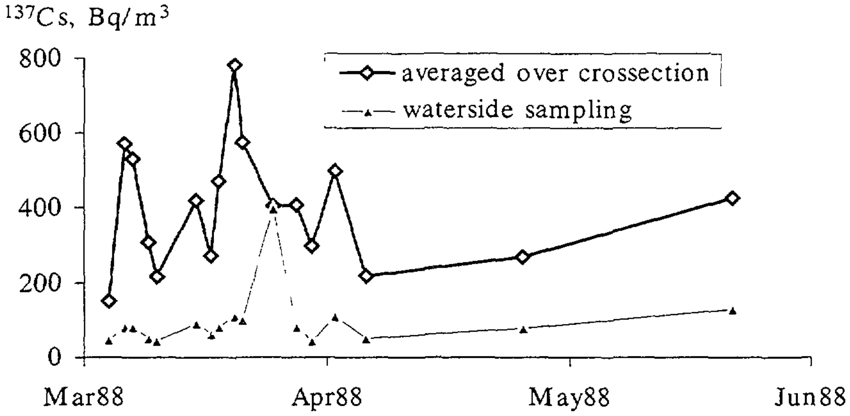

FIG 6. The comparison of ^{137}Cs concentration in the suspended sediments of riverside and averaged over the crossection samples, Pripyat-Chernobyl, 1988

In sampling of the suspended sediments for radionuclide analysys the important condition is the choosing of time interval sufficient to maintain smoothness of turbidity fluctuations. The sampling of the momentary sample can lead to the significant deviation of suspended sediments concentration in the sample from the mean value of turbidity in the river flux. The sampling technology "in situ" used by the Ukrainian Hydrometeorological Service excluded the influence of that deviation. So, the sampling of water samples from the Danube River by the filtration system MIDIYA during 2-3 hours are resulted in the averaging of turbidity and radionuclide concentrations along the jet in a few kilometres by length.

3. CONCLUSIONS

In conclusion it is necessary to note, that the Black Sea ecosystem is positively protected from the technogenic contamination from the Dnieper River. This protection are ensured by 6 large reservoirs, which are able to hold in its capacity the significant part of contaminants entered from the catchment.

To contrary, any technogenic accident on the Danube catchment can be accompanied by the transport of all quantity of the contaminants into the Black Sea. For revealing of the possible contamination and for the control of it movement along the river, as well as for the decision-making of the water protection measures it will be reasonable to create the common system of the water quality control over all the length of the Danube River. This system must be based, in the first turn, on the unified methods of water sampling and analysis.

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APPLICATION OF THE SPECTROMETRIC AND RADIOCHEMICAL TECHNIQUES IN ANALYZING ENVIRONMENTAL SAMPLES FROM THE BULGARIAN BLACK SEA REGION

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Abstract

Development of the appropriate methods and techniques for marine and atmospheric radioactivity measurements in the NIMH-BAS during the last 5 years is presented. Approaches for pre-concentration of the radionuclides from the atmosphere and sea water samples followed with reliable radiochemical methods for radionuclides separation and low level counting are discussed. Dissolved radiocesium concentrations measured in a period of time starting in 1993 show some decrease with years and spatial variations probably due to the hydrophysical features of the sampling sides - the lower measured concentrations during 1995 and 1998 correspond to the lower salinity. Application of the radiochemical separation of Plutonium, Thorium, ^{90}Sr and Americium on the samples from the Bulgarian Black Sea coastal region is reported.

1. INTRODUCTION

Although there are some investigations on the artificial radionuclides distribution over the Bulgarian coastal zone after the Chernobyl accident [1, 2, 3], a need for more extended information still exists. The influence of the Chernobyl accident on the radioactivity of the marine environment [4, 5, 6] require monitoring of the radioactive isotopes of Cs, Sr and Pu. Their utilization in hydrophysical studies is still an uncompleted task in Bulgaria. In the framework of the IAEA CRP "Application of Tracer Techniques in the Study of Processes and Pollution in the Black Sea" and TC project RER/2/003 during the recent 5 years the application of an appropriate methodology has been started.

2 METHODS FOR PRECONCENTRATION AND ANALYSES

2.1 Determination of Cesium isotopes in the surface waters

The concentrations of the ^{137}Cs and ^{134}Cs were determined in particulate matter, collected on the FPP filter (dried and pressed in 50cm^3 plastic container) and in the filtered water. Three methods were applied for determination of the dissolved Cs isotopes in the surface waters since 1993:

A.) Pre-concentration by evaporation; the method applied at NIMH for more than 20 years for determination of the ^{137}Cs in sea water [7]. In addition it was used for controlling the Cesium absorption under the sorbent method during 1993 and 1994.

B) High volume water samples collected by MIDIA filtration-sorbent system Extraction of Cesium is performed by fibrilose cationid CM-KI impregnated with copper ferrocyanide at a flow rate of 6-8 l/min for 200 to 600 l volume samples, after filtration on FPP filters The sorbent is dried and transferred to a plastic container (usually 0.451 Marinelli) for direct gamma counting by passive shielded 16.8% efficiency coaxial HPGe detector. The efficiency calibration of the spectrometer is performed under national calibration runs Different matrices are used by INRNE-BAS for preparation of the volume calibration sources with densities varying from of 0.35 to 2 g/cm^{3}by Measurements of the reference materials and participation in IAEA and national intercomparison runs was performed as a part of Quality control (IAEA-6, IAEA-307, IAEA-315, IAEA-300).

C) Co-precipitation of ^{137}Cs with AMP (Ammonium molybdophosphate). In brief the procedure includes acidification of the filtered sea water to pH1 with concentrated HCl , addition of stable cesium carrier (20mg) and ^{134}Cs tracer (15-30Bq), co-precipitation of cesium with AMP, dissolution of AMP in 10M NaOH and gamma counting. Chemical yield is determined by ^{134}Cs tracer activity in the sample compared to those in the standard solution, spiked with the same tracer activity.

Reliability and comparability of the results obtained during different years and expeditions were estimated by three approaches: comparison between method of evaporation and sorbent technique, analyzing parallel taken samples; duplicate sorbent samples (200, 300 and 600l) from a single site; duplicate sampling by sorbent technique and sample for AMP precipitation. The results are summarized in Table 1, where the ratio of activities and 2σ uncertainty of the parallel or consistent samples are presented. These results allow to say that the sorbent technique gives reliable and comparable values for ^{137}Cs concentrations in sea water, because of the close to 100% efficiency. One of the reasons for such high estimation is that we avoid ashing, which might cause the loss of 10-20% of the activity, according to [8]. The observed difference might be due to 2 reasons: a) the sorbent technique averaged the concentration of 3 to 10 times higher volume sample and b) systematic error of +10% in measured ^{137}Cs concentrations for sorbent is due to the calibration problem which might be solved after further preparation of lower density volume calibration source.

TABLE I. RATIO OF ^{137}Cs ACTIVITY AND 2σ UNCERTAINTY IN PRECONCENTRATED BY DIFFERENT METHODS SURFACE SEA WATER SAMPLES.

Sorbent to evaporated sample 1994	Sorbent to sorbent sample 1995, 1996	Sorbent to AMP sample
1.17±0.14	0.99±0.04	1.1±0.2
0.87±0.13[a]	1.04±0.05	1.2±0.2
1.26±0.23	0.98±0.06	

[a] In this case the sample for evaporation was not filtered. The activity of the ^{137}Cs in particulate matter was estimated to be 9% of the activity of the dissolved ^{137}Cs, measured in sorbent sample.

2.2. Sampling program. Pre-treatment of the biota, sediment and atmospheric samples.

The **sampling sites** were chosen between the coastal hydrometeorological stations to cover the all Bulgarian coast, see Fig. 1. These sampling stations are under the influence of the local anticyclonic vortex, formed in the area between the coast and the main Black Sea cyclonic current. Two stations, Shabla and Shkorpilovzi were pointed out as basic because of the available stable trestle bridges into the sea of 450 and 250m length, at the end of which the sea water and sediments were sampling.

Sea water, sediments and algae were sampling during the warm period of the year from May to September, usually during one day for every sampling station.

The **algae samples** were collected during every expedition along the coast, starting in 1993. The samples were rinsed with distilled water and dried at 105°C. Dry samples were milled and homogenized and measured for gamma emitting radionuclides. For radiochemical analyses ashing at 400°C was used. This temperature is lower than recommended for Pu and Sr analyses in [9], but it was chosen to have the possibility for additional gamma spectrometry measurement of the ashed sample. The registered loss of the ^{137}Cs was below 10%. The results are reported as Bq/kg dry weight. This year we have tried to obtain the ratio dry/wet weight for some of the species. The ratios are Ulva sp.- 0.2; Ceramium and Cystoseira sp.- 0.35, Phycoseris + Cladophora sp.- 0.25. These ratios are used in calculation of the Concentration Factors (CF) for ^{137}Cs. When it was possible an attempt to determine the species in old samples was done. The **fish samples** are treated similar to the algae samples. For the Trachurus sp. the head and internal organs are removed, for Sprattus sprattus the whole fish is treated. The **sediment samples** were collected from the surf zone. They are usually sandy for all sampling sides with different grain size. For comparability after drying they were sieved through 1mm sieve and two fractions ,<1mm grain size and >1mm were measured by gamma spectrometry.

Atmospheric deposition samples are collected at Varna and Burgas coastal stations every day by two types of collectors: 1) wetted with distilled water cotton material, which is dried, ashed with slow increase of the temperature up to 400°C, measured for gross beta radioactivity; 2) open container which bottom is covered by distilled water. Combined daily samples for a month period are measured by gamma spectrometry. Some of the monthly samples were analyzed for Plutonium, ^{90}Sr and ^{232}Th.

2.3 Radiochemical separation of Plutonium, ^{90}Sr and Thorium.

Two approaches in radiochemical separation of ^{90}Sr, $^{239+240}$Pu, Th and ^{241}Am were used. The first one is based on the classical ion exchange separation of actinides, and source preparation by co-precipitation with NdF_3, described in details in [10]. ^{90}Sr is determined through its daughter ^{90}Y according to [11]. For analyses of the atmospheric samples from the period of Chernobyl accident (collected daily or in several days period in May 1986) these procedures were combined [12], and further applied for monthly composed atmospheric deposition samples. The recovery for ^{236}Pu (later used ^{242}Pu) tracer was above 80%, for ^{90}Sr - from 70 to 85%, and for ^{243}Am - 40-68%. In algae and sediment samples actinides and ^{90}Sr analyses were performed on different subsamples. The blank samples were run in every series of analyses. ^{238}Pu was usually closed to the DL.

The latter developed procedure, permits determination of Pu, Th and ^{90}Sr in one sample, using new Eichrom Industries Inc. chromatographic materials - TEVA.Spec™ and Sr.Spec™. This procedure was applied on the soil samples first [14], recently on the some sediments from the surf zone. IAEA-6 and IAEA-307 were analyzed. Tracer only for ^{232}Th determination (^{230}Th presents as inpurity) was prepared by ^{234}Th milking from $UO_2(NO_3)_2$ dissolved in 7M HNO_3. The yield of the ^{234}Th is determined by gamma spectrometry with 25% Ge detector. The Thorium effluent after TEVA.Spec™ column is treated as Plutonium effluent. For further work the use of ^{229}Th is planned.

Alpha spectrometry was performed with 1 surface barrier detector in the beginning and since 1996 by OCTETE™ ORTEC alpha spectrometry system, EG&G ORTEC. The system includes eight 300mm^2 low level detectors from the series ULTRA-AS™ (100µm active layer thickness). Their background is <10imp/day. The usual FWHM for sources prepared by electrodeposition is 25-30 KeV, and for those by co-precipitation with NdF_3 vary from 50 to 120 KeV.

3. RESULTS AND DISSCUSSION

3.1. Levels of the ^{137}Cs along the Bulgarian Black Sea coastal zone

The averaged concentrations of ^{137}Cs in the **coastal waters** are presented in Table 2. ^{134}Cs determination was also possible in sorbent samples up to this year, clearly indicated for the Chernobyl influence. The concentrations in the period 1993-1998 are more then 10 times lower comparing to measured at the same stations in May 1986, [1] or to those presented in [4], [5]. The decrease is similar to the reported by [6] and [13].

TABLE II. AVERAGED CONCENTRATION OF ^{137}Cs AND ^{134}Cs, ONE STANDARD DEVIATION AND CONCENTRATIONS AND SALINITY RANGE IN SURFACE SEA WATERS

Month	^{137}Cs mBq/l	Range mBq/l	^{134}Cs mBq/l	Salinity range
Sep-94	41.7±3.4	38.2 - 45.1	1.39±0.08	16.4 aver.
May-95	33.1±0.8	32.1 - 33.9	0.74±0.12	16.3 - 16.6
Jun-95	34.9±3.5	32.4 - 41.1	0.94±0.12	14.7 -16.8
Jul-95	22.9±4.5	15 - 26.2	0.52±0.13	13.8 - 15.6
Sep-95	32.8±2.2	28.4 - 35.6	0.76±0.17	16.2 - 17.2
Summer-96^a	28±4	24 - 31.4	<0.5	16.1 - 17.1
June-98^b	20.5±2.8	18.2 - 24.3	0.20±0.05	15.5 - 17.1

^{a}Based only on the samples, collected in Varna; ^{b}Based on the samples from the Northern coastal region

On Fig. 1. the dynamic in ^{137}Cs concentrations in the surface water, obtained by sorbent technique during different expeditions for the period 1993-1998 for coastal stations Shabla and Shkorpilovzi are presented. The concentrations in both stations decrease approximately twice since 1993.

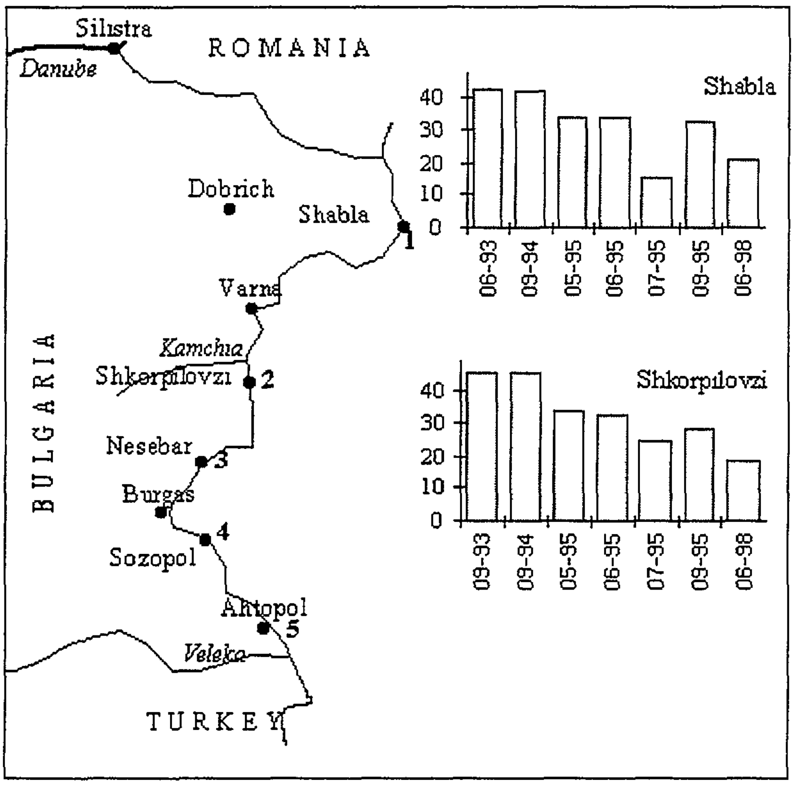

FIG. 1. Scheme of the sampling sites and ^{137}Cs concentrations in mBq/l in the surface water at two coastal stations. The basic stations are numbered 1-5.

The lower concentrations within one year correspond to the lower salinity, probably due to the refresh-ment caused by the inflow of the high Danube waters. ^{137}Cs concentrations measured during 1995 and 1996 in water samples from the Bulgarian part of the Danube river show almost an order of magnitude lower values - 0.4-0.8 mBq/l than those in the Black Sea surface waters. During June 1998 the growth of the salinity of the coastal water after strong storm was followed by a 25% increasing of the ^{137}Cs concentrations in 3 days period. The percentages of the ^{137}Cs associated with the particulate matter vary from 8.9 to less than 0.2%, depending mainly of the peculiar features of the sampling sites. The analysis of the ^{134}Cs/^{137}Cs ratio in collected sorbent samples discovers variations, but it is not so significant to exclude statistical variation. As an example, the average ratio for the 1995 for most northern station Shabla is 0.023 ($1\sigma=0.006$) and for Ahtopol it is 0.025 ($1\sigma=0.001$). The ration of 0.53 during the time of accident for the Black Sea, [4] recalculated for July 1995 gives a value of 0.024.

The data for ^{137}Cs concentrations in the surf **sediment** samples show smaller decrease during the period 1994-1998 in comparison to the concentrations in the sea water, but higher space variability, registered by [2] also. The concentration for Shabla (1) ranges from 1 to 1.8 Bq/kg dry weight for both <1mm and >1mm fractions, for the most southern Ahtopol (5) station from 3 to 4 Bk/kg. This fact corresponds to the values of Chernobyl fallout - deposited gross beta activity for Burgas bay region was 2 times higher and for Ahtopol station - 1.3 times higher than for North-East Bulgaria. These values in comparison to the concentrations of the natural gamma radioactive isotopes are low. ^{40}K in the region of Shkorpilovzi (2) vary from 60 to more than 100 Bq/kg. ^{226}Ra concentrations in the same samples vary from 3 to 14 Bq/kg.

The concentration of ^{137}Cs in **algae samples** also show space and time variability. For green algae (Ulva, Phycoseris and Cladophora species) the concentrations vary from 2.4 to 4.8 Bq/kg dry weight. For brown species (Ceramium and Cystoseira) usually higher concentrations are measured from 6 to 17 Bq/kg dry weight. The Concentration Factor, determined as CF=(Bq/kg)/(Bq/l) for the brown algae's samples is above 100 ranging from 170 in 1993 to 104 in 1998. For green algae species the averaged value is 34±18, within a range from 22 to 74. For both green and brown species higher uptake is observed in May and June, and lower in September.

3.2. Concentrations of other radionuclides in the samples from the coastal zone

The attempt to determine the dissolved **Radium** isotopes in the **coastal waters** , according to the method described in [14] was done in June 1998. Pre-filtered surface sea water sample (70 - 140 l) was passed through manganese oxides coated fiber (Mn-fiber) at a rate of about 0.2-0.5 l/min. The wet Mn-fiber was placed in a plastic 50cm^3 container and capped with a layer of silicone glue. No change of the weight of the container+sample was detected for 2 months' storage. The ^{226}Ra concentration was determined through ^{222}Rn daughters and ^{228}Ra through ^{228}Ac. The content of the Radium associated with the suspended matter was determined after gamma spectrometry of the filters used for pre-filtration. The volume of the filtered water was between 500 and 750 l. The concentration of the dissolved ^{226}Ra is estimated to be 1.5±0.3 mBq/l at Varna and 1.2±0.2 mBq/l at Shkorpilovzi, in agreement to the present concentration levels for the Black Sea, [15].^{228}Ra concentration is closed to 2mBq/l at both stations. The part of ^{226}Ra in particulate matter is 27 and 25% correspondingly.

The results for **$^{239+240}$Pu** (ion exchange resin) and **^{90}Sr** (by Sr.Spec^{TM}) are compared to previously analyzed **algae samples, Table 3.** The concentration of ^{137}Cs is also given. Both samples from 1995 were analyzed for ^{241}Am, but because of the low recovery (<50%) only the MDA - 0.05 Bq/kg could be reported. Again the brown Cystoseira demonstrate higher uptake than Ulva sp.

TABLE III. CONCENTRATION OF SOME ARTIFICIAL RADIONUCLIDES IN ALGAE SAMPLES

Species. Year of sampling. Station No.	$^{239+240}$Pu Bq/kg	Recovery in %	^{90}Sr Bq/kg	Recovery in %	^{137}Cs Bq/kg
Cystoseira sp., 1995 -5	0.12±0.02	62	7±1	55	17±1
Ulva sp, 1995 - 5	0.04±0.01	57	0.9±0.3	72	4.5±0.4
Cystoseira sp.*, 1988 - 4	0.15±0.1	72	9.5±0.4	76	15.5±0.5
Ulva sp.*, 1988 - 4	0.08±0.02	78	0.6±0.1	90.5	4.6±0.3

*analyzed in IAEA Seibersdorf Inter. Lab, J.LaRosa, A.Ghods, B.Veleva

The influence of **atmospheric deposition** on the marine environment in first approximation could be estimated from the deposition rate of the radionuclides at the stations situated near the sea. The recent deposition of ^{137}Cs over the territory of the North Bulgaria vary from <0.5 to 20 mBq/m^2 per day. During 1996 the averaged value at Varna station is 2.5 mBq/m^2 per day and at Burgas - 3.5 mBq/m^2 per day. On Table 4. the averaged deposition of $^{239+240}$Pu, ^{90}Sr, ^{137}Cs and ^{232}Th for 2 months is given. On coastal station Varna higher $^{239+240}$Pu deposition rate was detected, but for the other reported radionuclides the values are similar to the measured in the interior.

TABLE IV. ATMOSPHERIC DEPOSITION OF $^{239+240}$Pu, ^{90}Sr, ^{137}Cs AND ^{232}Th

Sampling station	Period of sampling	$^{239+240}$Pu mBq/m^2 per day	^{90}Sr mBq/m^2 per day	^{232}Th mBq/m^2 per day	^{137}Cs mBq/m^2 per day
Varna	Oct-92	0.033±0.006	NA[a]	0.03±0.01	5.2±0.6
Musala peak	Oct-92	0.0026±0.0007	2.9±0.2	0.026±0.009	8±1
Varna	May-95	0.0065±0.0012	0.4±0.1	<0.02	4±1
Pleven	May-95	0.0032±0.0013	2.6±0.6	NA	12±2
Sofia	May-95	0.0016±0.0006	2.3±0.3	NA	NA

[a] The sample is not analyzed for this radionuclide

4. CONCLUSIONS

During the period of the investigation (1993-1998) ^{137}Cs concentrations in the surface water along the Bulgarian shore have decreased. The refreshment by high Danube waters in late spring and early summer can cause additional decreasing in ^{137}Cs concentration, especially at the Northern stations. The tendency of decreasing is observed in the surf sediment and algae samples, as well.

The brown algae species demonstrate higher uptake of $^{239+240}$Pu, ^{90}Sr and ^{137}Cs compared to the green ones and could be used as biomonitors for the Northern Black Sea coastal region.

The methods for determination of $^{239+240}$Pu, ^{90}Sr and gamma emiting radionuclides in the Bulgarian coastal environment have been developed and applied in the NIMH and INRNE-BAS laboratories. The support in capacity building received under TCP RER/2/003 is playing a significant role in the process of development. The results obtained under the application of these methods are considered reliable and could be used in further monitoring studies.

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PRESENT LEVEL OF CONTAMINANTS IN THE ROMANIAN BLACK SEA SECTOR

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Abstract

The assessment of environmental quality in the Romanian Black Sea sector is being constantly made by the Romanian Marine Research Institute (RMRI) within the National Integrated Monitoring System. The contamination of the marine environment is expressed by considering four chemical and a biological parameter: nutrients ($N–NO_2$, $N–NO_3$, $N–NH_4$, $P–PO_4$, organic P, $Si–SiO_4$), heavy metals (Mn, Fe, Cu, Cd, Pb), artificial radionuclides (^{90}Sr, ^{137}Cs), total hydrocarbons, parasite and saprophyte fungi in sediments, sea water and/or biota. Present levels of contaminants are discussed as to their historical evolution during the last few years or decades. Inorganic N and P concentrations still exceed three to five times those before eutrophication started to intensify in the early '70s. Practical uses of results by national and regional authorities are discussed.

1. INTRODUCTION

The north–western sector of the Black Sea covers 63,900 km^2, with a depth less than 200 m, and it is directly influenced by the freshwater contribution from the Danube, Dniester and Dnieper (85% of the total); the hydrographic basin of those rivers amounts to about 1.4 million km^2, representing a catchment area by five times larger than the marine area they flow into. The Azov Sea mainly receives the waters of the Don and Kuban, as well as from three other smaller rivers.

The Romanian marine coast is 245 km long. Ten cities/towns and 100 rural localities amounting to about 650,000 inhabitants have developed along the littoral. They represent 8% of the population of the Danube basin (which is almost a half of the collectivity of the entire Pontic basin).

The climatic conditions depend on the season, and oscillate from the summer heat (25.5°C) to winter cold (down to –8°C). The wind force and direction are variable in time, the north winds are predominant during the cold season, and the south winds – during the warm season. The monthly averages of the severe winds in winter range from 4.7–7.1 m/s. The strong storms (with winds exceeding force 8) have a reduced frequency.

The development of the industrial and agricultural activities, the intensification of the river and maritime goods traffic in the Black Sea basin, as well as the population increase have caused an increase in pollution with dramatic effects on the coastal zone and marine ecosystem. It is well known that up to the beginning of the '90s, only the Danube contribution exceeded 34,000 t of mineral N, 60,000 t of total P, 6,000 t of Zn, 1,000 t of Cr, 280 t of Cd, 60 t of Hg and 50,000 t oil.

Besides erosion, the Romanian littoral as a whole has been affected by the high eutrophication of the coastal waters directly resulting in the alarming decrease of its biodiversity.

2. MATERIAL AND METHODS

The research regarding the evolution of environmental quality along the Romanian littoral is permanent within the framework of a general physico–chemical and biological monitoring programme.

More than 30 parameters are usually investigated as a consequence of the existing pollution sources (the influence of the Danube and other rivers, industrial and domestic sewage, port activities, intense tourism areas). Among these four chemical and a biological parameters have been analysed, namely: main nutrients ($N–NO_2$, $N–NO_3$, $N–NH_4$, $P–PO_4$, organic P, $Si–SiO_4$) in sea water, heavy metals (Mn, Fe, Cu, Cd, Pb) and artificial radionuclides (^{90}Sr, ^{137}Cs) in sediments, sea water and biota, total hydrocarbons in sea water, and parasite and saprophyte fungi.

The samples have been periodically collected from a network of stations off the Romanian coast, from various locations, depths and seasons, depending of the pollutant. The **nutrients** in the Danube water and coastal sea water have been analysed by using methods described by [1]. The **heavy metals** have been determined by atomic absorption using a spectrophotometer ATI–UNICAM, type SOLAR 9392, provided with a Zeeman correction cell and a system for automatic data recording and processing [2, 3]. Radiochemical separation of **^{90}Sr** and gamma spectrophotometry for **^{137}Cs** have been used for analysing the radioactivity of marine emerged and submerged sediments, water and biota: macrophytes, invertebrates, fish [4]. The UV spectrophotometric method (270–320 nm) for the liquid–liquid samples (sea water – 3 hexane7dichloromethane) has been used for **hydrocarbon** determination; the calibration has been carried out with Danube Reference Oil [5, 6, 7]. Several methods [8, 9, 10, 11, 12] have been used for quantitative and qualitative estimate of the **fungi** belonging to the phylum Mycophyta.

3. RESULTS AND DISCUSSION

3.1. Nutrients

The Black Sea receives a big volume of freshwater containing considerable amounts of inorganic nutrients. Owing to a strong thermohaline stratification and to a long residence time of water masses, the Black Sea ecosystem is highly sensitive to increased production of organic matter. The last thirty years represented a period of high intensification of the anthropogenic pressure on the coastal environment and high eutrophication, with negative effects on the whole ecosystem. Important nutrient and organic inputs from rivers and industrial and domestic drainage resulted in the increase of the magnitude and frequency of algal blooms followed by hypoxia and anoxia, benthic mortalities and a remarkable decrease of biodiversity. As the main current direction in the area is southward, the Romanian shelf representing 40% of the total shelf of the Black Sea is the most affected area. It receives water from the rivers Danube, Dnieper and Dniester, and the Danube contribution exceeds 70% of the total volume. The annual Danube water discharge between 1931 and 1995 indicates significant fluctuations and decadal trends, in addition to the expected seasonal variability. These fluctuations have therefore a major influence on the nutrient budgets of the western shelf water.

The annual nutrient loads, derived from the monthly averages of nutrient concentrations and water discharge, also displayed interannual changes. The data obtained at Sulina between 1988–1996 show that the Danube drained 4.1–8.1 x 10^5 t/year of dissolved inorganic nitrogen into the Black Sea, with a percentage of nitrates exceeding 90%. During 1980–1986, the annual phosphate and silicate loads in the Danube were of 0.06–0.33 x 10^5 t/year and 1.5–5.0 x 10^5 t/year, respectively.

A comparison with other data [13] shows that DIN discharge increased by a factor of 4 to 5, and phosphorus load increased more than 2 times. At the same time the silica discharge from the Danube was reduced very much. For the last 15 years, the annual average discharge of silica was less than a half of the estimated silica input before 1970. This fact has been related to the decrease of the solid river discharge, as a consequence of the damming works for energy production upstream the river and its tributaries, and of its intense consumption during the previous massive diatom blooms as well. A seasonal prevalence of the nutrient stocks followed the water discharge.

Considering the interannual changes of the nutrient stocks discharged by the Danube into the sea, a slight but continuous diminishing tendency should be noticed after 1990 (Fig. 1).

On the Romanian shelf, the highest nutrient stocks were reached in the '70s, they decreased considerably in the '80s and have slightly diminished during the '90s (Fig. 1). Even if a decrease tendency has been recorded during the last two years, the content of inorganic nitrogen salts is still high, exceeding by 3–5 times the levels before the eutrophication. The phosphorus values were similar to those before the eutrophication and it frequently reached the exhaustion stage. High N:P ratios (different from Redfield oceanic model) strongly suggest phosphorus as the nutrient with limiting role for the Romanian shelf waters [14]. The decrease of silica concentrations has been much more evident and is actually three times less than during the reference periods.

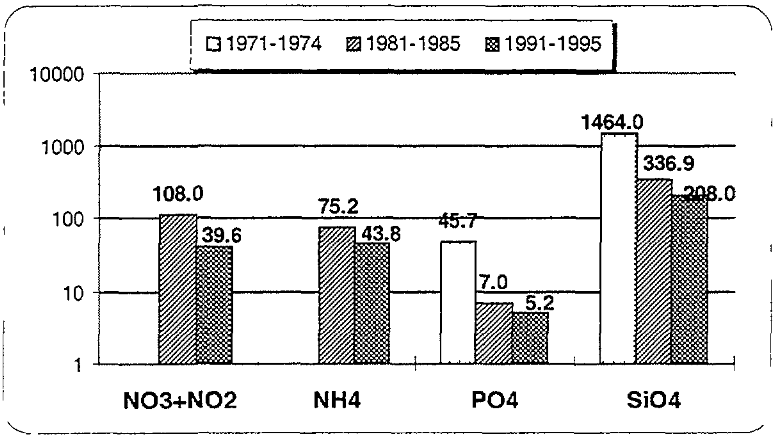

FIG.1 Time evolution of the nutrient stocks on the Romanian shelf (thousand tonnes)

3.2. Heavy metals

The control of environmental quality of the Romanian coast is achieved by a permanent monitoring of Mn, Fe, Cu, Cd and Pb.

In the northern sector, the content of heavy metals in sediments ranged between 2.43–4.24 µg/g Mn, 48.23–61.38 µg/g Fe, 14.71–17.89 µg/g Cu and 11.57–18.91 µg/g Pb. In the sea water, the heavy metal concentrations oscillated between 2.79–25.03 µg/g Mn, 30.36–193.8 µg/g Fe and 3.11–17.54 µg/g Cu. These values are rather high, the Danube influence being strong in the marine environment.

For the southern sector, the heavy metal content in sediments is higher than in the sea water: 18.6–284.88 µg/g Mn, 244.33–426.47 µg/g Fe, 21.52–360.56 µg/g Cu, 0.13–3.98 µg/g Cd and 3.93–131.3 µg/g Pb. Many of the maximum values have been found in Constanta port area and especially at berth 34 (Petromar), and most of the minimum values – offshore at a depth of 70 m. The maximum values were comparable with those found in front of the Danube mouths. For the coastal waters, the values were of 0.17–172.8 µg/L Mn, 0.41–417.8 µg/L Fe, 5.27–28.93 µg/L Cu, 5.82–17.67 µg/L Cd and 1.48–12.08 µg/L Pb. For depths of 10 m, the heavy metal contents were 0.35–13.20 µg/L Mn, 1.83–26.51 µg/L Fe, 0.39–20.37 µg/L Cu, 0.59–10.08 µg/L Cd and 2.15–4.79 µg/L Pb.

Among the marine biota, the mussels from Vama Veche (4.5–5.0, 5.0–5.5 and 5.5–6.0 cm) and several fish species from Mamaia Bay have been analysed. For mussels, the heavy metal contents were of 46.13–92.28 µg/g fresh weight Mn, 118.43–176.4 µg/g Fe, 16.66–22.45 µg/g Cu, 10.03–30.76 µg/g Cd and 4.44–9.36 µg/g Pb. The fish samples had heavy metal concentrations of 4.47–5.85 µg/g dry weight Mn, 52.86–66.18 µg/g Fe, 11.24–17.86 µg/g Cu, 13.62–16.77 µg/g Cd and 4.01–5.56 µg/g Pb.

As far as the heavy metal concentrations in sea water along the Romanian littoral are concerned, the concentrations of Fe, Cu and Pb either at the seashore (0 m) and at a depth of 10 m are lower when compared with other areas of the World Ocean. An exception is Cd, with values in shallow waters exceeding greatly those in other areas. The content of heavy metals is within the maximum limits of the Romanian standards for seawater: 300 µg/L for Cu, 30 µg/L for Cd and 50 µg/L for Pb [15].

3.3. Radionuclides

The radiometric investigation of the coastal marine ecosystem [16, 17, 18] was continued in 1997; the results showed the presence of the long–lived anthropogenic radionuclides ^{90}Sr and ^{137}Cs.

Significant ^{90}Sr activities (1.53–7.64 Bq/kg dry) were found in the emerged marine sediments collected from seven profiles between the northern and southern limits of the Romanian littoral. The maximum value was recorded at Chituc, station 2 (33.8 m depth).

In the surface seawater, ^{90}Sr content varied over a very narrow range, 19.18–21.83 Bq/m^3. During 1993–1997, this radioisotope varied between rather constant limits. The mean activity of ^{90}Sr was close to the mean value identified by other researchers studying the Black Sea waters [19] during 1975 and 1988–1991.

The green and red macrophytes had a ^{90}Sr content of 0.37–1.08 Bq/kg fresh weight, both maximum and minimum values measured in the green alga *Enteromorpha linza*. The molluscs samples represented by two bivalves and a gastropod had very low activities of ^{90}Sr, namely <0.13–0.28 Bq/kg f.w., of which 50% were below the detection limit. The maximum concentration of ^{90}Sr was determined for the bivalve *Mytilus galloprovincialis*. The measurement of ^{90}Sr in the most frequent benthic fish species collected resulted in significant values of 0.63–0.98 Bq/kg f.w. The maximum concentration was recorded for *Gobius melanostomus*, 24% higher than the values obtained for the same species in 1994 and 1995.

The numerous investigations carried out on environmental pollution up to 10 m depth in 1997 indicated ^{137}Cs concentrations of 6.6–86 Bq/kg dry in sediments collected from the southern coast. The maximum value was found off the Danube mouths. The local variations are remarkable and correlate with the hydrodynamic conditions and sediment quality, a fact which could explain the minimum value found in a nearshore area. The observations were extended along the entire coast in bottom sediments up to 70 m depth, resulting in radionuclide concentrations of up to 249 Bq/kg dry; the maximum value found at a depth of about 50 m indicated that other marine processes or phenomena may have been involved (e.g. sediment transport). The most recent analyses carried out on the emerged sediments showed low concentrations (at an average less than 5 Bq/kg f.w.). The fine beach sediments in the Constanta area did not exceed 10 Bq/kg f.w. The determination of ^{137}Cs concentration in a reference sea water sample (Constanta, offshore) showed a concentration of 0.036 Bq/L, close to the value of 52 Bq/m^3 recommended by [20]. Marine biota had low ^{137}Cs concentrations of only a few Bq/kg f.w. The macrophytes had a radionuclide content of 0.7–0.8 Bq/kg f.w. (maximum value for *Ceramium rubrum*). For molluscs, it varied between 0.4 and 1.9 Bq/kg f.w., with maximum values recorded in *Mya arenaria* and *Mytilus galloprovincialis*. Rather significant values were found for fish, where the ^{137}Cs concentrations ranged between 1.4 and 3.4 Bq/kg f.w., with the maximum value measured in *Sprattus sprattus phalericus*.

3.4. Hydrocarbons

Hydrocarbon monitoring was based on the analytical results of the total hydrocarbon content determined in sea water from the areas exposed to loading with oil polluting agents.

The spatial distributions of the concentrations in the river water and sea water demonstrate the impact of the river discharges estimated at 328.4 µg/L in 1997. The contributions of the river inputs located in the northwest Black Sea contaminated by oil exploitation activity and naval traffic cause the significant increases of the hydrocarbon loading at 20 m depth.

The pollution from oil decreased in 1995–1997, and the lowest values were recorded in 1997 [21], when that contamination was reduced by 4.2 times off the Sulina Channel and by 10.3 times off the Danube mouths marine area.

Between Navodari and Vama Veche, the results obtained in 1997 showed a pollution level of 91.4–1029 µg/L near the shore and 49.3–183.9 µg/L in offshore waters at 0–10 m depths; the spatial distribution of the hydrocarbon concentrations in that area of the coast illustrates the effect of the water treatment mainly along the depths of 0 m, where the mean pollutant loading is 67.3% higher than the mean value for the offshore area.

During 1995–1997, the temporal variability of hydrocarbon pollution was characterized by a reduction over time [21, 22].

3.5. Fungi

In time the mycological data from the shallow water area have shown the importance of this biological indicator of pollution. Certain groups of saprophyte and pathogenic micromycetes are indesirable as they endanger the sanitary condition of these waters including the bathing waters. The negative aspect of the excessive development of the mycoplankton resulting in "fungi blooms" concerns its quantitative and qualitative development.

The representatives of family Cryptococcaceae have been found permanently in the polluted water masses; they have become predominant and have generated ample "fungi blooms" caused by the genera *Candida, Rhodotorula, Cryptococcus* and *Trichophyton.* The strictly marine taxa belonging to the family Thraustochytriaceae were identified for the first time in Romanian sea waters [10] and then were found frequently in small quantities.

In comparison with the degree of fungus pollution in coastal waters for 1990–1997, and previous investigation periods, some slow but continuous changes have been noted concerning both the structure and dynamics of fungi by the exclusive proliferation of some pathogenic yeast fungi. For example, in 1997 an explosion of the reproduction elements (conidia, blastospores, arthrospores, bud cells) was noticed at Mamaia, Constanta South and Vama Veche in comparison with the previous years. During the same year, at the 10 nautical miles Tuzla reference station the fungi increased considerably and generated a *Geotrichum candidum* bloom.

4. CONCLUSIONS

1. The highest N and P stocks recorded in Romanian shelf waters in the '70s decreased considerably during the '80s but only slightly during the '90s; inorganic salt concentrations still exceed three to five times those existing before eutrophication began to intensify (1970).
2. Phosphorus values similar to those before eutrophication and the high N:P ratio suggest P as a limiting nutrient in the shelf waters.
3. Present silicon concentrations have apparently decreased as much as threefold compared to the afore mentioned reference period.
4. High concentrations of some heavy metals in Romanian littoral sediments including those in Constanta South area are mainly due to land based pollution sources (point sources, water treatment stations, port activities).
5. The ^{90}Sr content in marine biota is relatively low (maximum 1 Bq/kg fresh weight).
6. The highest values of ^{137}Cs are found in the submerged sediments (maximum about 200 Bq/kg dry).
7. Concentrations of ^{137}Cs in marine biota are a few Bq/kg f.w., and vary according to taxonomic group.
8. The temporal variation in hydrocarbon pollution demonstrates the anthropogenic input to the environment.
9. Off the Danube mouths, the mean concentration of oil of 170 μg/L is 42% higher than that determined for the southern part of the littoral at depths of 10 m.
10. Fungus pollution has increased with a predominance of the family Cryptococcaceae.
11. Many of the *Rhodotorula* species, found in 60% of the analysed samples, are pathogenic followed by the species belonging to the genera *Candida*, *Cladosporium* and *Penicillium.*
12. There are sensitive seasonal quantitative differences in the specific structure of the mycoplankton, among which the spring–summer species of the genera *Trichoderma* and *Epicoccum* are more important.
13. The potentially pathogenic yeast fungi have particularly proliferated reaching very high levels in all locations over the last few years.
14. The "fungi blooms" have been produced by the filamentous complex *Penicillium – Cladosporium* and pathogenic yeast complex *Rhodotorula – Candida – Geotrichum – Cryptococcus* off the localities most affected by waste overflows, namely Mamaia, Eforie North and Mangalia.
15. These results can be used as a support for environmental protection measures recommended by the Ministry of Waters, Forests and Environmental Protection and its subordinated organisms (Environment Protection Agency, "Romanian Waters"), requests of the Danube Delta Biosphere Reserve Authority through research projects, Black Sea Strategic Action Plan and fulfilment of Romanian obligations within the framework of the Convention on the Protection of the Black Sea Against Pollution (Bucharest Convention, 1992) and Odessa Ministerial Declaration (1993).

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OXYGEN-18, DEUTERIUM AND TRITIUM IN THE BLACK SEA AND THE SEA OF MARMARA

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Abstract

The stable isotopes oxygen-18 ^{18}O and deuterium ^{2}H, as well as tritium ^{3}H transient tracer were used to study pycnocline and deep mixing, to identify water masses in the Marmara and Black Seas, and to characterise exchange through the Turkish Straits System.

1. INTRODUCTION

The stabilising effects of excess fresh water and two-layer stratified exchange through the Turkish Straits System have led to anoxic conditions below the pycnocline in the Black Sea with partial renewal through the Bosphorus. While the ventilation of the upper pycnocline is driven by turbulent convection, it occurs through cascading of the shelf-mixed Mediterranean water at the continental slope [1-3], and double diffusive convection [4-7] mechanisms in the lower pycnocline. The post-Chernobyl radioisotopes [8], ^{14}C [9, 10] and tritium [11] measurements were consistent with the above results, showing very little penetration below a depth of about 500 m, and increasing age of waters near the bottom. On the other hand, the Marmara Sea has a mean residence time of a few months for surface waters, and about 6 years for the deep waters [13, 14]. Radioisotopes have been used widely for mixing and transport studies in the Black Sea [15-18].

We report on recent measurements of ^{18}O, ^{2}H and ^{3}H from samples collected in March-April, 1995, along the continental shelf and deep waters of the western and southern Black Sea (Fig. 1) and in the middle of the Marmara Sea, aboard the R/V BİLİM of the IMS-METU. Of the 11 stations in the Black Sea, 6 were sampled down to a depth of 150m, 4 stations extended to 250m, and deep samples down to 1500m could only be obtained at a single station. The three stations in the Marmara Sea extended to 1200m. Other details of the sampling and analyses were given in [19,20].

2. STABLE ISOTOPES ^{18}O AND ^{2}H

Mixing between the *i.e.* the Mediterranean and the Black Sea waters is well reflected in the stable isotope data, with sharp contrasts across the pycnocline and constant levels in deep waters of both seas (Fig. 2). Freshwater influence from major rivers (Danube, Dniepr and Dniestr) in the northwestern shelf region of the Black Sea results in decreased $\delta^{18}O$ and $\delta^{2}H$ values near river mouths and along the shelf [20]. There are large horizontal and vertical variations within the thin (20m) upper layer of the

Marmara Sea, as a result of entrainment and mixing between Black Sea and the Mediterranean waters. In general, our results are similar to those of [16, 17], and [21], but contain much less noise. The sub-halocline (Mediterranean water) $\delta^{2}H$ variance in the Marmara Sea is slightly larger than the $\delta^{18}O$ variance, in contrast to [21].

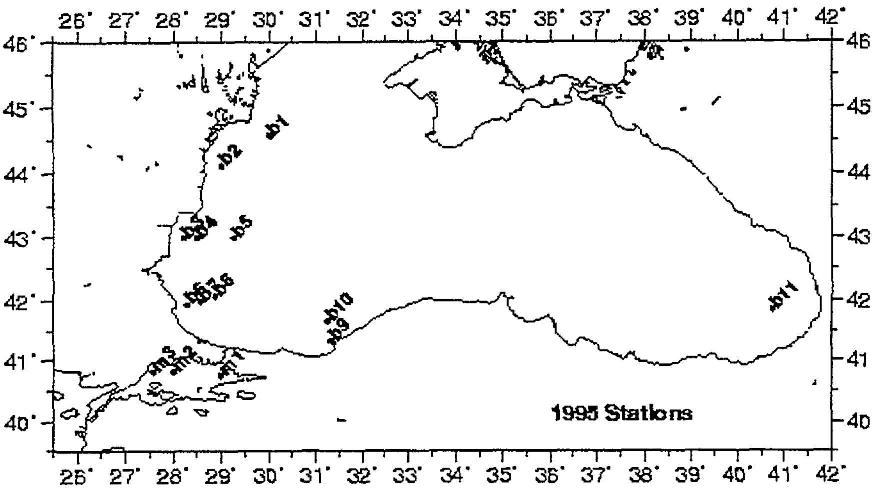

Fig. 1. Black Sea and Marmara Sea stations in 1995.

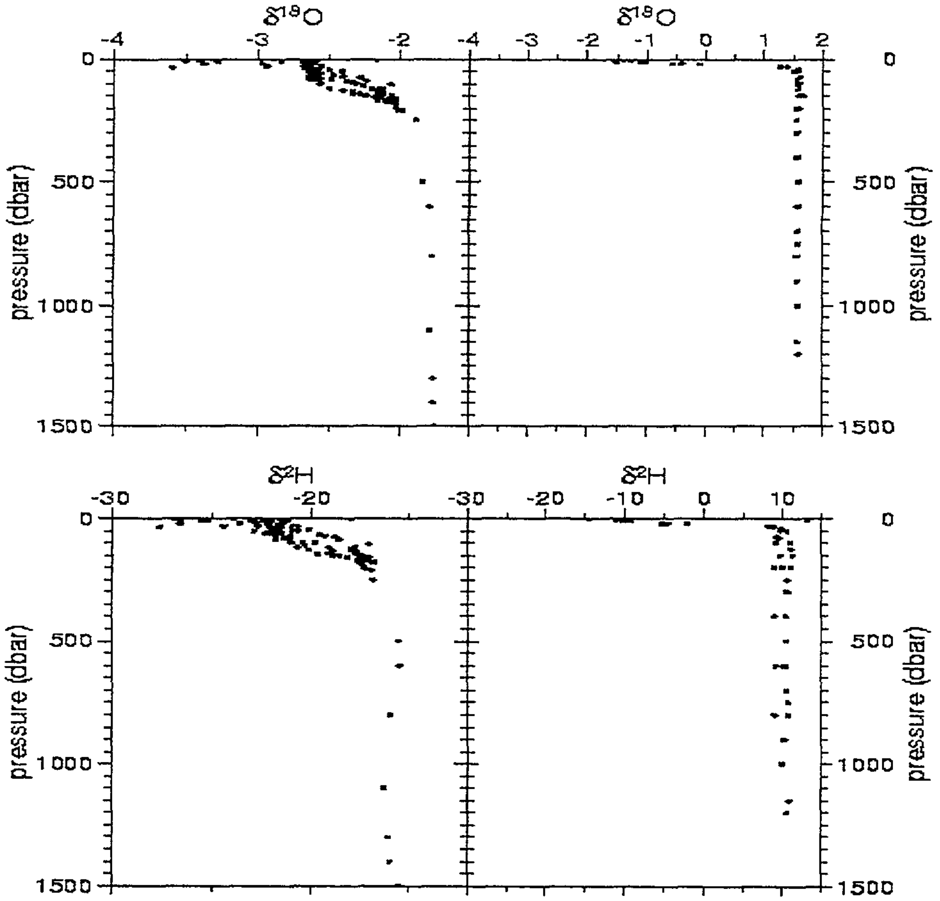

Fig. 2. Vertical distribution of stable isotopes in 1995; left: Black Sea; right: Marmara Sea; top: $\delta^{18}O$ measurements; bottom: δ^2H measurements.

3. TRITIUM

In the Black Sea, below the pycnocline, where the tritium decreases rapidly below 500m to very low values near the bottom. Although we only have data from one deep station in 1995, it is evident that the concentrations decrease to almost zero in deep water, within the precision of the measurements. In the Marmara Sea, only very small variations, typical of the efficiently ventilated Mediterranean region, occur below a depth of 25m.

The tritium distribution in the lower layer of the Marmara Sea has a maximum at mid-depths and possibly a slight increase near the bottom. These slight variations in the small basin indicate local changes in relative age, depending on seasonal, transient renewals by intrusions of Mediterranean water [13, 14] which are also evident in the salinity and temperature fine structures. We observe that δ^2H and ^3H have slightly larger variability compared to $\delta^{18}O$ in the subhalocline waters. Our ^3H measurements appear to have less scatter than the earlier measurements, and clearly demonstrate physical variations.

4. DENSITY DEPENDENCE

Because mixing between the surface and deep waters is limited by stratification, the dependence between chemistry and physical mixing of scalar properties produces self-similar profiles [22, 7], especially in the lower part of the pycnocline where turbulence rapidly declines. The linear dependence of stable isotopes versus σ_θ density (Fig. 4) eliminates the effects of dynamical displacements, and implies that the water mass evolution has followed the history of contact with the atmosphere. This is an independent verification of a hypothesis of deep water mass formation by a mixture of Mediterranean and near-surface, relatively fresh water masses, based on temperature -salinity analyses alone [3, 5], and the late quaternary history of Black Sea [23, 24].

In contrast, the transient tracer tritium versus σ_θ density in Fig. 4, indicates a significant change in tritium gradient with respect to density is evident below the pycnocline. Especially the fact that the break appears in the transient tracer and not in the stable isotopes shows that bomb tritium from the atmosphere has not yet been able to penetrate into the deeper Black Sea, and that the efficiency of penetration sharply decreases below the pycnocline, $\sigma_\theta \cong 16.3$. This result must reflect different mechanisms of renewal for intermediate and deep waters explored in a number of earlier interpretations [3, 5], *i.e.* turbulent mixing above the pycnocline, and rapidly diminishing turbulent mixing replaced with lateral intrusions of Mediterranean water below the pycnocline, extending down to a depth of about 500m or $\sigma_\theta \cong 17$. Indeed, below 500m, there is very little tritium.

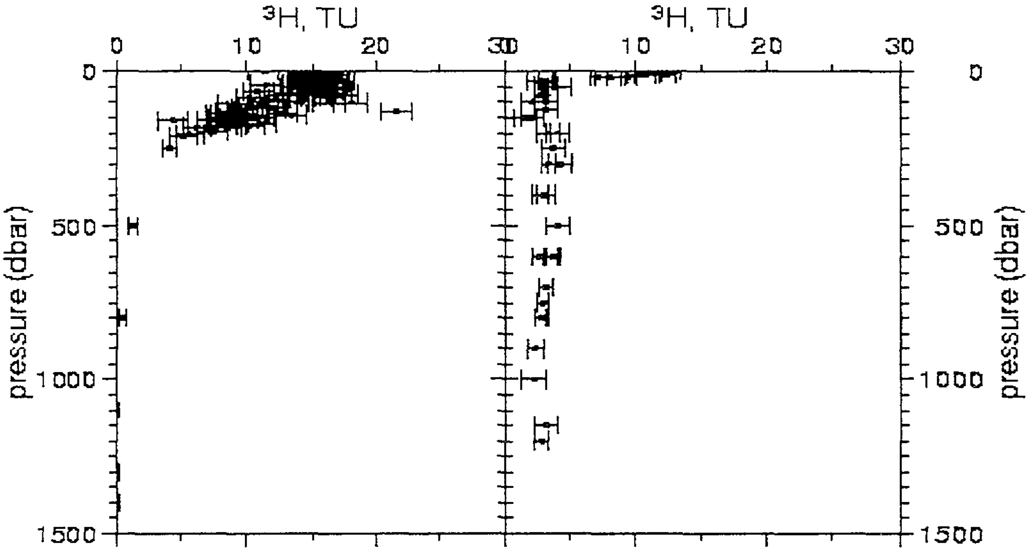

Fig. 3. Depth profiles of ^3H measurements, 1995. left: Black Sea; right: Marmara Sea; error bars show σ resulting from measurement uncertainty.

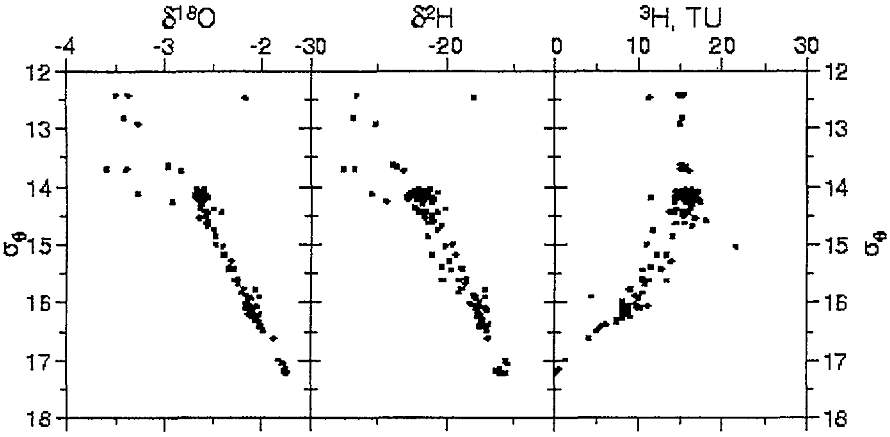

Fig. 4. Profiles of stable isotopes and tritium as a function of σ_θ *density in the Black Sea. left:* $\delta^{8}O$; *center:* $\delta^{2}H$; *right:* ^3H.

4. SURFACE TRANSIENTS

The $\delta^{18}O$ for the Danube in Vienna [25, 26, 27] has a mean value of -11.5 %oO, and a range of -10.3 %oO to -13.3 %oO %oO. The average value near the mouth of the Danube is about -10.5 %oO. Stable isotopes within the upper 20m waters of the two seas, appear to have rather small seasonal and interannual variations, based on measurements in 1988 and 1993 [16].

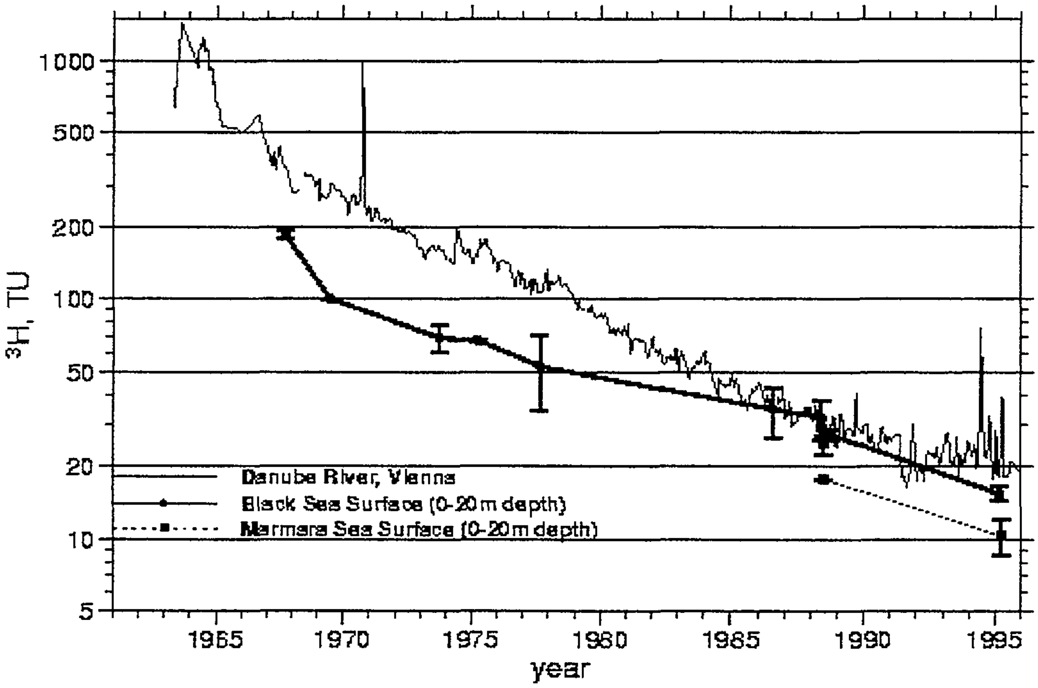

Fig. 5. Surface ^3H *concentrations measured in the Black Sea and Marmara Sea surface layers (0-20m depth), superposed on a plot of* ^3H *measurements in the Danube River. Danube samples were obtained at Reichsbruecke (before Dec 1991), and Nussdorf-Schleuse (after Dec 1991) in Vienna.*

The transient tracer tritium in precipitated water, the Danube waters [25, 26, 27] and the surface waters of the two seas has been decreasing since the 1963/64 maximum in fallout (Fig. 5), in agreement with other observations (*e.g.* [28]). The present input to the Black Sea is about 10-15 TU from precipitation (1995) and 20-25 TU from Danube water. This is at present on the same order of magnitude as the ^{3}H of Black Sea surface waters (15-17 TU). The comparison of riverine sources and surface marine observations indicate this difference to be larger in the 1960's and 1970's (Fig. 5), when the inputs were considerably larger but the underlying waters were less contaminated.

In the case of Marmara Sea waters, there is a larger difference in surface tritium concentrations with respect to the input functions. Despite the smaller size of the Marmara Sea, mixing with the underlying Mediterranean waters yields a further dilution in the surface waters. The main part of this mixing is believed to occur at the Bosphorus Strait and its exit region in the Marmara Sea (*e.g.* [12, 14]).

5. EXCHANGES BETWEEN BASINS

The average surface and deep properties and the inter-basin exchange characteristics are schematized in Fig. 6, based on average surface levels and those measured below a depth of 500m in the Black Sea and 50m in the Marmara Sea. The fresh water inflow, specifically from the Danube river, entering the sea with a low δ^{18}O, has a significant influence in the northwestern shelf region, where it lowers the δ^{18}O. The deep water of the Black Sea, with a historical Mediterranean contribution, is enriched in terms of δ^{18}O. In contrast, the recent source of tritium at the surface has not been able to penetrate into the deep waters, the ^{3}H values decreasing rapidly below a depth of 500m. In the Marmara Sea, the ^{18}O and ^{2}H characteristics of surface waters evolve rapidly at the transitions across the Bosphorus and Dardanelles Straits, and from west to east by mixing with underlying Mediterranean waters. The subhalocline Marmara waters essentially bear the same signature as the Mediterranean waters.

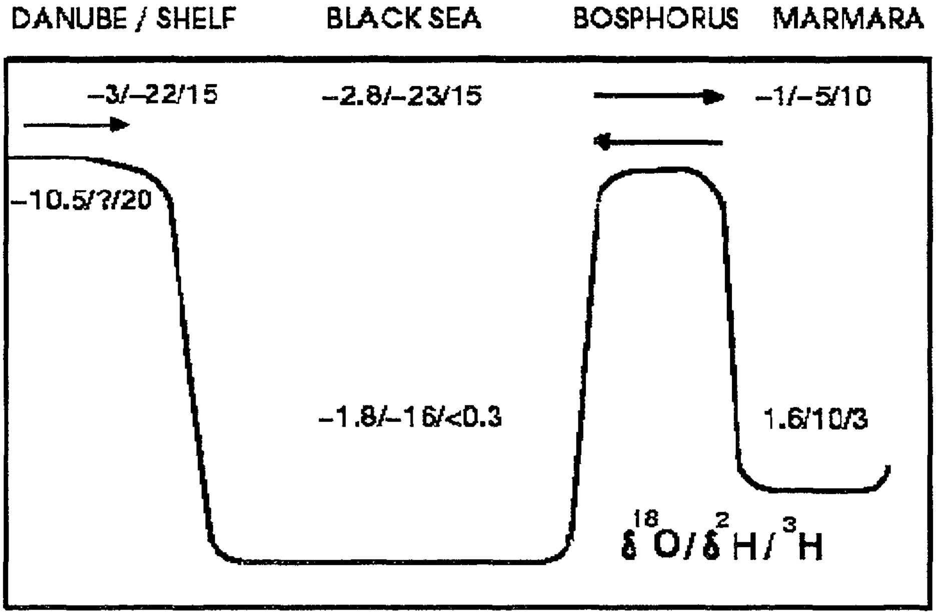

Fig. 6. Idealised surface (depth 0-20m) and bottom (depth >500m in the Black Sea, and depth >50m in the Marmara Sea) concentrations of isotopes, $\delta^{18}O/\delta^{2}H/^{3}H$*, in the Danube river (Vienna), the northwestern shelf area, greater part of the Black Sea, and the Marmara Sea.*

6. ISOTOPIC CORRELATIONS

Fig. 7 correlates all three isotopes studied. In the upper panel we observe that all the data in the two interconnected basins of Marmara and Black Sea to lie along the same straight line, slightly displaced from the meteoric water line, and with only a minor change in slope between basins, suggesting that these waters were formed by a continuous mixture of fresh water inputs and Mediterranean water. Mediterranean water in the Marmara Sea has slightly higher δ^2H, compared to the Eastern Mediterranean [21].

In the oxygen-18 versus tritium plot (lower part of Fig. 7), Marmara and Black Sea data are located along different branches, as a result of differences in residence time of the deep waters in the two basins. The transient tracer tritium indicates age, while the oxygen isotope, is linearly related to stratification, and measures distance from the conditions determined by surface hydrology. The near-surface waters in the Black Sea form a cluster of rather uniform values; while a group of points displaced to the left from this cluster, and belonging to the northwestern shelf region is helpful in identifying

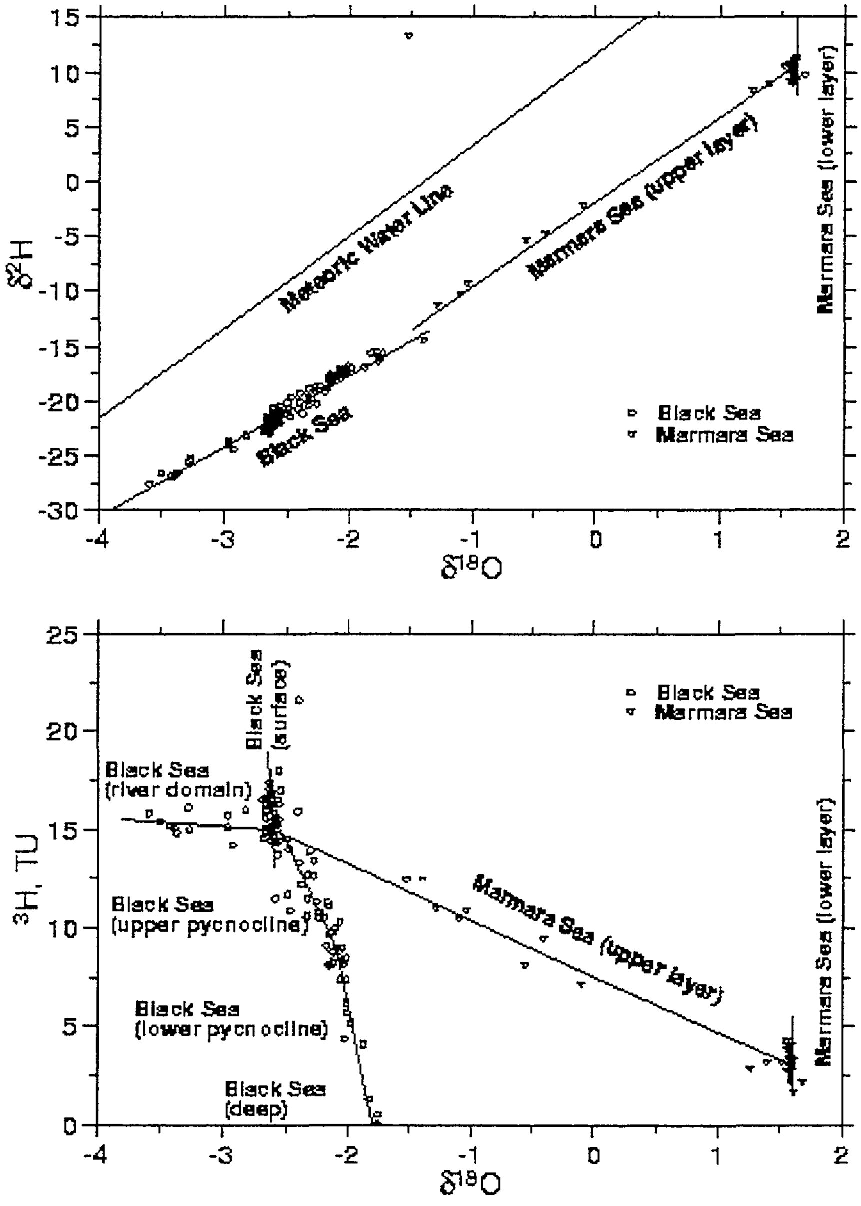

Fig. 7. top: $\delta^{18}O$ versus $\delta^{2}H$, bottom: $\delta^{18}O$ versus ^{33}H for the Black Sea and Marmara Sea, 1995.

riverine effects. Fresh water is tagged by the oxygen isotope, but not by tritium, which is similar in all surface samples. Below the surface, tritum decreases and oxygen increases with depth. In the Black Sea, we observe that there is a well defined change of slope occuring immediately below the pycnocline, clearly showing that two different mechanisms are responsible for the renewal of the water masses above and below it.

7. CONCLUSIONS

The use of stable isotopes together with transient tracers in the Black Sea and Marmara Sea has yielded new results which help to understand the mixing and renewal in these semi-enclosed basins of greatly differing characteristics.

Stable isotope measurements in precipitation and river runoff, characterising fresh waters and the atmosphere, are relatively constant in time, and their ratios help identify mixing between waters with different origins. In the region studied, there is nearly a linear correlation between oxygen and deuterium for all water samples, showing that the waters in both basins are continuously proportional mixtures of surface fresh water inputs to the Black Sea and salty waters of the Mediterranean.

In the Marmara Sea, stable isotopes at the surface evolve rapidly at the transitions across the Bosphorus and Dardanelles Straits, and in an east to west direction in the Marmara Sea interior by mixing with the lower layer Mediterranean waters. Both isotopes show very little change below 500m in the Black Sea, and below 25m in the Marmara Sea, consistent with hydrographic observations, showing common sources.

On the other hand, tritium is decreasing in precipitation, river runoff and the surficial waters of Black Sea and Marmara Sea, consistent with fallout and decay. Mixing with underlying waters determine the delayed response of the Black Sea and Marmara Sea surface waters, which differ in their settled characteristics. The surface and deep waters in both Seas are separated by a sharp pycnocline identified in all three tracers. Stable isotopes have a continuous linear dependence on density, while tritium shows a discontinuous dependence showing different renewal mechanisms for deep and intermediate waters.

River (freshwater) influence is identified along the western Black Sea continental shelf, on the basis of isotope correlations. Tritium measurements show a rapid decrease across the Black Sea pycnocline, and constant levels below the pycnocline in the Marmara Sea. Comparison of tritium with stable isotopes can characterize all distinct water masses in the two basins.

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IAEA-SM-354/28

CHRONIC OIL POLLUTION IN THE BOSPHORUS, SEA OF MARMARA AND DARDANELLES

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Abstract

Oil pollution was measured at the entrance and exit of the Bosphorus and Dardanelles monthly and seasonally at two stations in the Black Sea and four stations in the Sea of Marmara in 1995-1996. In 1996, the oil level increased; in the Bosphorus, in the surface water, 4.8 times at the entrance, 2.9 times at the exit, in 10 m 3.2 times in the entrance, 9.2 times in exit, in the Sea of Marmara 2.8 times in the surface water, 42.9 times in 10 m. In the Dardanelles 8.3 times at entrances and 7.7 times at the exit and in 10 m 2.5 times at the entrance and 5.3 times at the exit. The results showed that the pollution has increased in the Turkish Straits throughout the years.

1. INTRODUCTION

The Turkish Straits comprise of the Istanbul Strait (the Bosphorus), Çanakkale Strait (the Dardanelles) and the Sea of Marmara. The water exchange between the Black Sea and the Mediterranean Sea takes place through these straits. There are two currents in these straits, the upper current is the Black Sea water which flows into the Sea of Marmara at a rate of 0.5-4.8 knots and the under current is the Mediterranean Sea which flows into the Black Sea at a rate of 1.6 knots.

Petroleum hydrocarbons are important contaminants in the seawater. In the Bosphorus, the origin of the oil pollution is mainly the Black Sea, in which 410000 t/a of oil is being discharged [1]. In the Sea of Marmara, the pollution is caused by the inflow from the Black Sea and heavy marine traffic and also the refinery located in Izmit Bay [2].

The oil pollution in these straits had not been measured before the Nassia accident which occurred in 13 March 1994 and the results were published [3, 4].

In this paper, oil pollution was reported in the Black Sea (7 miles, near the Bosphorus), in the Bosphorus, the Sea of Marmara and in the Dardanelles between 1995-1996.

2. MATERIAL AND METHODS

The sampling stations are shown in Fig.1. Surface water samples were taken in the Black Sea near the Bosphorus at 2 stations in 1996 and northern entrance and southern end in the Bosphorus and Dardanelles in 1995-1996, in the Sea of Marmara at 4 stations in 1995-1996.
The pollution measurements were made monthly in the Bosphorus and Dardanelles and seasonally in the Black Sea and in the Sea of Marmara.

The seawater samples were taken at the surface in 3L amber glass bottles held by special holders. In seawater samples 15 ml dichloromethane (DCM) was added immediately for preservation .

2.1 Oil concentration measurement

The oil concentration was determined in a 2.8L seawater sample. The extraction was made three times with 50 ml DCM. The extracts were combined, dried over anhydrous sodium sulphate and distilled under vacuum. The residue was dissolved in hexane and the volume adjusted to 10 ml with hexane. The hydrocarbons concentration was measured in UV spectrofluorophotometer (UVF) using standard curve [5]. The calibration curve was plotted using Russian crude oil in concentrations of 0.25, 0.50, 1.00 and 1.50 µg/ml in hexane and the measurement was made at 310/360 nm (ex/em) in UVF (Shimadzu, RF-1501).

(1) GC/MS analysis:

GC/MS analysis was run by a HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD) controlled by HP ChemStation. Operating conditions were: 50 mx0.20mm fused HP PONA, methyl siloxane, glass capillary column; oven temperature programme; 40°C at 6 min, from 40-280°C at 10°C/min, 280°C at 10 min, from 280 -290°C at 10°C/min, 290°C at 5 min; splitless injector temperature 300°C; carrier gas helium.

3. RESULTS and DISCUSSION

The equation of the calibration curves of Russian crude oil is as follows:
$F1 = 590.74\,C + 38.711,\ r^2 = 0.9998$

TABLE I THE CONCENTRATION OF OIL IN EXAMINED STATIONS

		at surface water	at 10 m depth
Black Sea		1996; 32.6µg/L	1996; 13.70µg/L
Bosphorus;	northern entrance	1995; 5.53 µg/L	1995; 3.56µg/L
		1996; 27.0 µg/L	1996; 11.70µg/L
	southern end,	1995; 13.6 µg/L	1995; 5.52µg/L
Sea of Marmara;		1995; 36.9 µg/L	1995; 3.84µg/L
		1996; 103.7 µg/L	1996; 164.90µg/L
Dardanelles;	northern entrance,	1995; 5.24 µg/L	1995; 14.39µg/L
		1996; 43.5 µg/L	1996; 36.00µg/L
	southern end,	1995; 5.29 µg/L	1995; 5.49µg/L
		1996; 40.9 µg/L	1996; 29.60µg/L

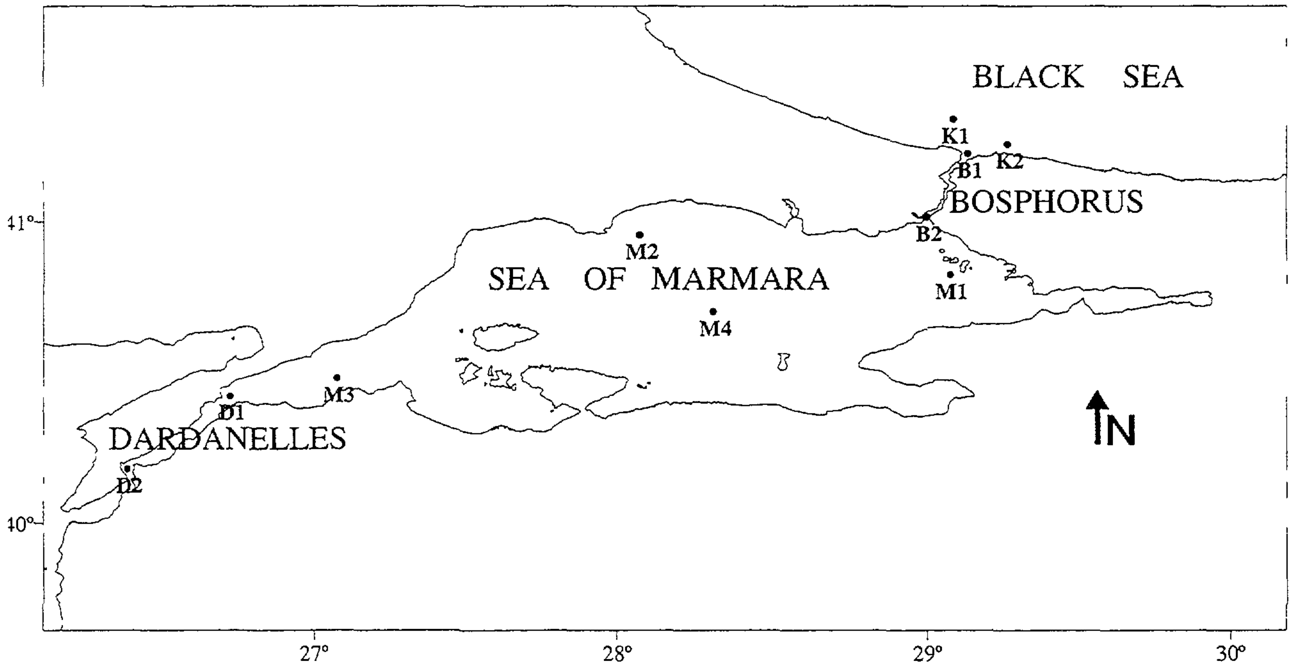

FIG. 1: Sampling stations

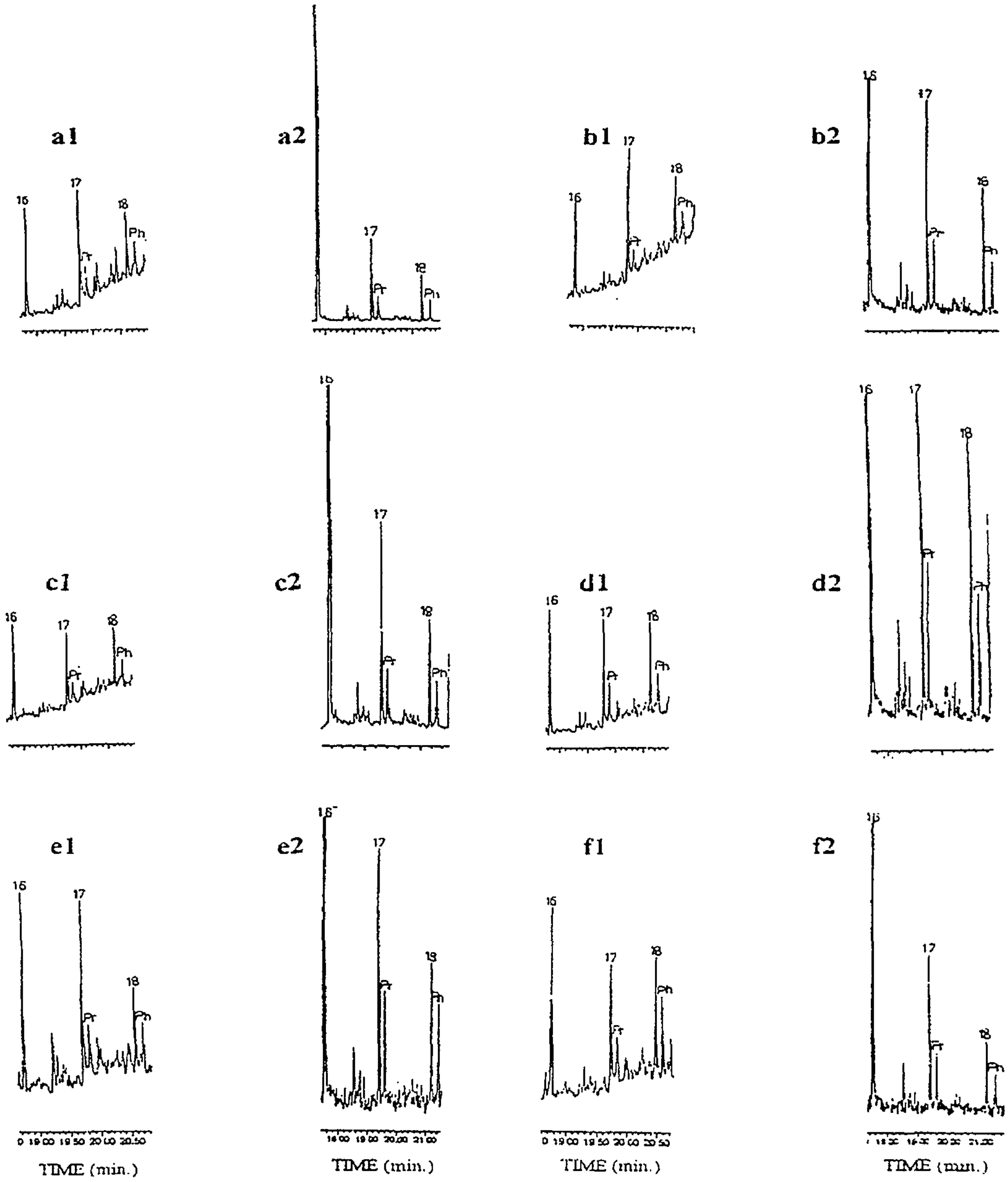

FIG.2. GC/MS chromatograms of surface water
The Bosphorus: entrance ***a1*** *1995,* ***a2*** *1996: exit* ***b1*** *1995,* ***b2*** *1996*
The Dardanelles: entrance ***c1*** *1995,* ***c2*** *1996: exit* ***d1*** *1995,* ***d2*** *1996*
The Sea of Marmara: ***e1*** *(M4) 1995,* ***e2*** *(M1) 1996,* ***f1*** *(M3) 1995,* ***f2*** *(M3) 1996*

In 1996, the similarity was found in the oil levels of the Black Sea and entrance of the Bosphorus and also in 1995-1996 at the entrance and exit of the Dardanelles at surface water and 10 m depth samples but not in the samples of Bosphorus. There was not found any similarity in the Sea of Marmara. The comparison of the oil levels in 1995-1996 shows that the oil concentration increased in 1996.

The selected GC/MS chromatograms are shown in Figure 2. No difference was found between the GC/MS chromatograms of the Bosphorus and the Dardanelles samples. In the GC/MS chromatograms the observed peaks are Pristane (Pr) and Phytane (Ph) in 6, 7/1995, and 6, 11/1996 (month/year). Pr/Ph ratios are lower than one (0.56-0.98). This finding indicates that the origin of hydrocarbons is petrogenic [6]. Unresolved complex mixture (UCM) observed in all chromatograms indicated recent oil pollution in the sampling stations [7].

TABLE II. OIL AMOUNT OF THE SEAWATER (µG/L) İN SURFACE WATER (A) AND AT 10M DEPTH (B)

i- BLACK SEA

		The Black Sea			
Year	Station	K1		K2	
	Month	a	b	a	b
1996	2	3.08	3.72	2.38	3.83
	5	1.65	4.96	1.49	8.35
	8	9.85	11.7	7.96	13.7
	11	32.6	10.0	11.2	12.3

ii- BOSPHORUS AND DARDANELLES

		Bosphorus				Dardanelles			
Year	Station	B1		B2		D1		D2	
	Month	a	b	a	b	a	b	a	b
1995	5	5.53	-	5.59	-	-	-	-	-
	6	5.29	-	5.52	-	-	-	-	-
	7	4.42	-	4.02	-	5.24	4.64	4.11	4.39
	8	3.28	2.78	3.00	1.61	5.00	2.09	5.29	3.27
	9	1.97	2.63	4.06	3.80	3.43	4.85	2.32	5.49
	10	3.23	1.55	13.60	5.24	2.70	14.39	1.95	3.25
	11	3.66	3.18	12.10	5.25	2.99	3.72	4.29	2.76
	12	4.18	3.56	3.74	5.52	4.08	4.47	3.51	4.18
1996	1	2.51	-	13.1	3.74	3.23	3.91	2.42	2.80
	2	2.66	2.57	19.1	7.14	1.99	3.92	4.52	4.20
	3	4.00	8.46	4.40	4.19	3.99	4.74	2.61	3.78
	4	5.00	3.00	4.49	4.38	4.82	3.30	6.43	3.41
	5	1.35	8.00	10.5	12.40	5.75	4.82	29.3	27.4
	6	16.4	-	37.4	24.30	29.6	7.74	17.2	10.1
	7	7.85	-	11.6	18.50	5.53	9.96	8.80	6.51
	8	22.1	11.7	33.2	27.30	9.73	9.59	40.9	28.1
	9	27.0	-	30.8	51.10	31.3	32.7	27.7	29.6
	10	10.1	-	39.5	26.30	43.5	36.0	22.3	26.0
	11	11.9	10.0	12.1	13.50	12.1	29.6	12.8	12.2
	12	3.57	-	2.78	2.32	26.9	10.51	6.91	6.25

iii- THE SEA OF MARMARA

		The Sea of Marmara							
Year	Station	M1		M2		M3		M4	
	Month	a	b	a	b	a	b	a	b
1995	7	4.15	-	3.65	-	3.65	-	4.47	-
	11	4.80	3.00	4.30	4.40	35.26	3.40	36.9	3.84
1996	2	2.06	3.00	-	-	-	-	-	-
	5	-	-	4.18	1.09	4.23	9.26	3.59	1.96
	8	8.00	11.30	-	-	-	-	-	-
	9	-	-	103.7	164.9	-	-	-	-
	10	-	-	-	-	40.7	50.9	41.2	54.5
	11	-	3.26	-	-	-	-	-	-

The Black Sea is polluted mainly from Danube, Dniester, Dnieper etc. rivers flow, municipal and industrial waste water [8] and also from the oil products delivered in to the Black Sea [1]. Additionally shipping activities involving tankers are the major sources of the oil pollution in the Bosphorus and the Sea of Marmara.

When compared the oil pollution of Turkish Straits with the Black Sea; Alusta (1991) 50 µg/L, Sevastopol (1990) 540 µg/L, Yalta (1991) 180 µg/L [9], Novorossisyk-Gelendzhik area 130 µg/L [9], the Bosphorus; (B2), 92.8 µg/L and in the Sea of Marmara; (M2); 103.7 µg/L show that the oil pollution is lower in the Bosphorus (except Alusta). Seasonal variation of the oil concentration in the Turkish Straits depend on the temperature and the oil level in winter and spring increased while in summer decreased.

In this study the concentrations of oil in the Turkish Straits seawater were generally all in excess of 13 µg/L, stipulated by FAO(1989) and hence are classified as polluted (Table II).

The highly dynamic nature of water movement and mixing in the Turkish Straits especially in the Bosphorus as indicated above is likely to be the main factor in promoting natural dissipation of the spilled oil. The renewal of surface water of the Bosphorus is approximately daily whereas this process takes three months in the Sea of Marmara. The high petroleum pollution in the Sea of Marmara caused by the inflow from the Black Sea, the very high marine traffic and the İzmit refinery is aggravated by the low current velocity of the Marmara seawater.

These findings showed that the oil pollution in Turkish Straits increased throughout the years.

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THE DYNAMICS OF NUTRIENT ENRICHMENT AND PRIMARY PRODUCTION RELATED TO THE RECENT CHANGES IN THE ECOSYSTEM OF THE BLACK SEA

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Abstract

During the spring period of 1998, light penetrated into the upper 25-35m, with an attenuation coefficient varying between 0.1 and 0.5 m^{-1}. The chlorophyll-a (Chl-a) concentrations for the euphotic zone ranged from 0.2 to 1.4 $\mu g\ l^{-1}$. Coherent sub-surface Chl-a maxima were formed near the base of the euphotic zone and a secondary one was located at very low level of light in the Rim Current region. Production rates varied between 450 and 690 $mgC/m^2/d$ in this period. The chemocline boundaries and the distinct chemical features of the oxic/anoxic transition layer (the so-called suboxic zone) are all located at specific density surfaces; however, they exhibited remarkable spatial variations both in their position and in their magnitude. Bioassay experiments (using extra NO_3, NH_4, PO_4 and Si) performed during Spring 1998 cruise showed that under optimum light conditions the phytoplankton population is nitrate limited in the open waters. Phosphate seems to control the growth in the Rim Current regions of the southern Black Sea. Si concentration also influenced the phytoplankton growth since the majority of the population was determined as diatom.

1. INTRODUCTION

The Black Sea is a relatively large, deep, landlocked anoxic basin and there exists a permanent and strong halocline at depths of >50-200 m, shoaling in the central cyclones and deepening in the coastal regions. Continuous downward transport of biogenic particles from the productive surface layer, combined with limited vertical ventilation through the permanent halocline are the major reasons for the anoxic conditions in the deep waters. The presence of cyclonically meandering Rim Current along the peripheries of the basin partly isolates coastal waters from the interior waters. The Black Sea is further unique possessing very narrow shelf along more than half of its margin, except northwestern shelf area.

In addition to natural biochemical processes forming the anoxia in the deep waters, the increasing input of nutrients and organic matter from land-based sources during the last two decades, generated dramatic changes in the Black Sea ecosystem, especially in the wide northwestern shelf [1-5]. Long-term modifications and collapses of the biological structure of the ecosystem have been well documented [3,6,7]. However, the lack of good quality historical data of high resolution impairs understanding of how the recent anthropogenic inputs and climatic changes have influenced nutrient and organic carbon pools of the Black Sea. Nevertheless, comparison of the limited earlier measurements with the high-resolution data obtained since 1988 has enabled several workers to address the magnitude of the long-term changes in the nutrient and oxygen profiles from the upper layer down to the sulphide-bearing waters of the deep basin [9 - 15]. Similar changes have been observed in the nutrient chemistry of the waters of the northwestern shelf [5].

Primary production in the Black Sea displays two phytoplankton maxima throughout the year; the major one occurs in early spring while a secondary peak appears in autumn [16,17]. Recently, additional summer blooms have frequently been observed in both the coastal and open waters [18,19,20,21]. Primary production is relatively low in the open sea (50-200 gC m^{-2} y^{-1}) compared to the northwestern shelf area (up to 400 gC m^{-2} y^{-1}) [2,17], where there are riverine discharges of nutrients[5]. Since input of nutrients from the anoxic layer through the permanent pycnocline is limited both by denitrification and by oxidation-reduction processes occurring in the oxic/anoxic transition layer, since the major nutrient source for the open system is the input from the nutricline [22]. New production in the open waters of the Black Sea is therefore dominated by the input from the nutricline, riverine input via surface circulations and atmospheric transport probably being of secondary importance; consequently the rates of new production in the Black Sea are low [22,23].

2. RESULTS AND DISCUSSION

Area of Study: The station network for Spring 1998 cruise is illustrated in Fig. 1. Previous studies clearly demonstrate the physical oceanography of the Black Sea upper layer to be dominated by the quasi-permanent cyclonic gyres in the eastern and western halves of the basin. The two gyres are separated from a series of anticyclonic eddies in the coastal zone by the cyclonically undulating Rim Current [24]. The influence of the freshwater input, mainly from the Danube, Dnepr and Dnester rivers at the northwestern shelf, can be traced down to the Bosphorus region [20]. The stations were selected according to such physical structures.

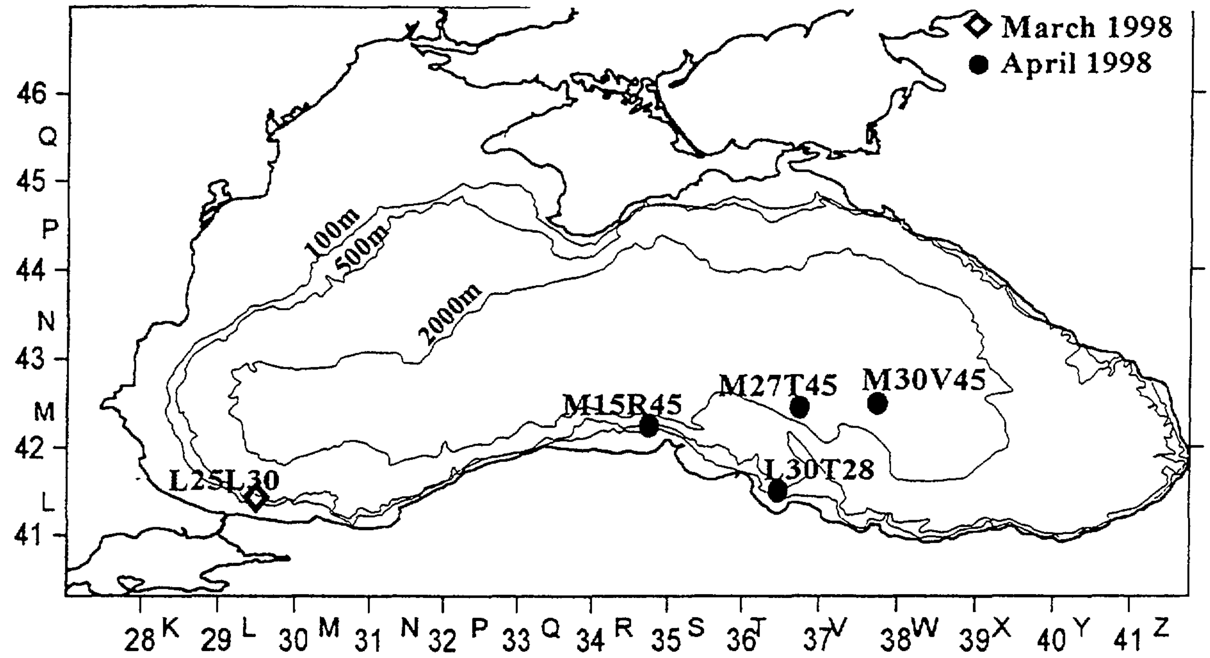

FIG. 1.Station network for the spring 1998 cruise

Hydrographic Structure: The profiles of Temperature, Salinity, Density (Sigma-theta = σ_t) and Light Transmission from the southern Black Sea demonstrate that a nearly isohaline and relatively cool, isothermal water mass exists below the seasonal pycnocline (Fig. 2). This prominent and persistent feature of the Black Sea, termed as the Cold Intermediate Layer (CIL), possesses a temperature minimum which is characterized by the 8 °C limiting isotherms [24]. The thickness of the CIL is larger (up to 100m) in the anticyclonic regions (ACYC) than in the cyclonic regions (CYC) (about 50m). The σ_t =14.8 isopycnal surface defines not only the temperature minimum within the

CIL but also the upper boundary of the permanent pycnocline in the Black Sea [10]. In the CIL, the salinity varies slightly from nearly 18.5 to 20.1 ppt. The profiles illustrated in Fig. 2 show that, in March 1998, when the surface waters cool down to 7 °C, the upper layer is thoroughly homogenized - by convective mixing down to the σ_t = 14.7-14.8 isopycnal surfaces. With the advent of heating in the early spring, the surface temperatures rise to 12-13°C and then CIL becomes topped by a warm surface layer (Fig.). Below the CIL the temperature gradually rises from 8 °C to 8.7 °C at the base of the permanent pycnocline; this is observed at different depths for different regions. The subhalocline waters posses similar temperatures at similar density surfaces over the basin though isohalines appear at different depths from the deep to the coastal region. The light transmission is between 75-90% down to the lower boundary of the CIL and it increases to higher percentages or transmission down to σ_t =16.0-16.2 where the fine particle layer is located with low transmission.

Chemical Properties. The chemical profiles down to the anoxic waters were plotted relative to water density and depth as a vertical scale for selected stations. (Fig. 3.) AS recently indicated, composite profiles from hydrodynamically different regions exhibit characteristically similar vertical features below the euphotic zone down to the upper anoxic layer when the vertical scale is density [14,15,22].

Dissolved Oxygen (DO). Fig.3 shows the surface layer down to the temperature minimum the CIL to be nearly saturated with dissolved oxygen(DO=300-350 μM). The concentrations decrease steeply in the upper depths of the permanent pycnocline from 300 μM at the σ_t =15.5 surfaces, these surfaces defining the upper and lower boundaries of the main oxycline. As recently indicated [25], the oxycline commences at greater density surfaces (σ_t =14.4-14.5)but at shallower depths 950-60m) in cyclonic regions than in the frontal zones of the Rim Current or in anticyclonicregions where the onset is located at σ_t =114.2-14.3 970-100m) Below the main oxycline DO declines slowly to <20μM at σ_t =15.9-16.0 and can no longer be detected at the σ_t =16.15-16.20 density surfaces where sulphide concentrations are 1-3 μM (Fig. 3). This DO-deficient water, formed within the oxic/anoxic transition layer with DO <20 μM and H_2S <1 μM, is called the suboxic zone. Sulphide-bearing waters were consistently observed at density surfaces of >16.15-16.2 over the entire deep basin. In the upper anoxic layer, the H_2S concentration increased steadily with depth, showing insignificant spatial or temporal variation at any density surface.

Phosphate (PO_4) and T-NO_x (NO_3+NO_2) Distributions: As previously emphasised [15,21], the surface waters of the southern Black Sea are always poor in nutrients during the seasons when these waters are stratified. In the late spring 1998 when the seasonal stratification has started to established, concentrations in the euphotic zone were less than 0.5 μM for T-NO_x (mainly NO_3), 0.35 μM for phosphate and 5 μM for Silicate. The nutrient data from previous years [21,26] together with modelling studies [23] indicate that intense vertical mixing in winter provides input from the nutricline which may increase surface nitrate concentrations 5-10-fold. Composite profiles of T-NO_x and phosphate indicate that, below the euphotic zone, nutrient concentrations increase with increasing density down to the base of the main oxycline (Fig. 3). The nitrate concentrations display a well-defined maximum of 5-8 μM at 15.5 density surface defining the upper boundary of the suboxic zone where DO concentrations decrease to 20-30 μM. In the suboxic zone, due to denitrification, nitrate concentrations decline steadily to 0.1-0.2 μM at the suboxic/anoxic interface. Nitrate then becomes reduced by sulphide in the upper anoxic waters until to undetectable levels. Phosphate concentrations increase within the oxycline to a maximum in the upper suboxic zone or at the σ_t = 15.6-15.7 isopycnal surfaces. Below this broad maximum, phosphate concentrations decline steeply in the cyclonic regions, forming a pronounced minimum (0.05-0.10 μM) at the σ_t = 15.9-16.0 isopycnal surfaces. This feature is less marked in coastal regions and it is nearly imperceptible within the Rim Current region. Nevertheless, throughout the deep basin phosphate profiles always increase steeply within the sulphidic water interface and reach peak values of 6-8 μM at σ_t = 16.2 isopycnal surface. Phosphate concentrations decrease slightly in the upper anoxic layer and then increase again slightly with depth. The occurrence throughout the deep basin of the marked maximum at the sulphidic boundary probably results from dissolution of phosphate-associated Fe- and Mn-oxides in the anoxic waters [13,27]. Silicate concentration increase steadily below the euphotic zone with increasing depth and density.

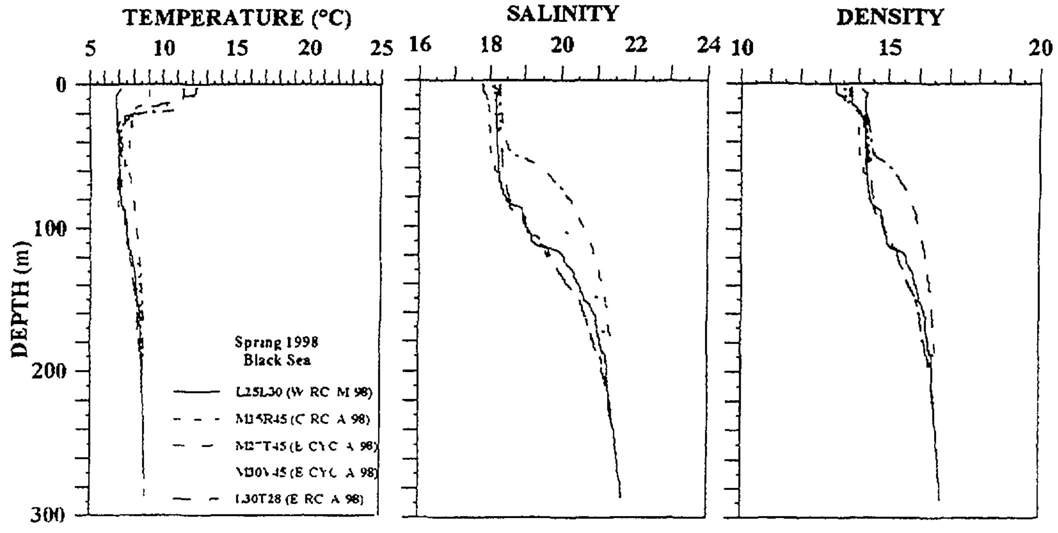

FIG 2 Potential Temperature (°C) Salinity and Sigma-theta (Density) Profiles in the southern Black Sea for Spring 1998 period

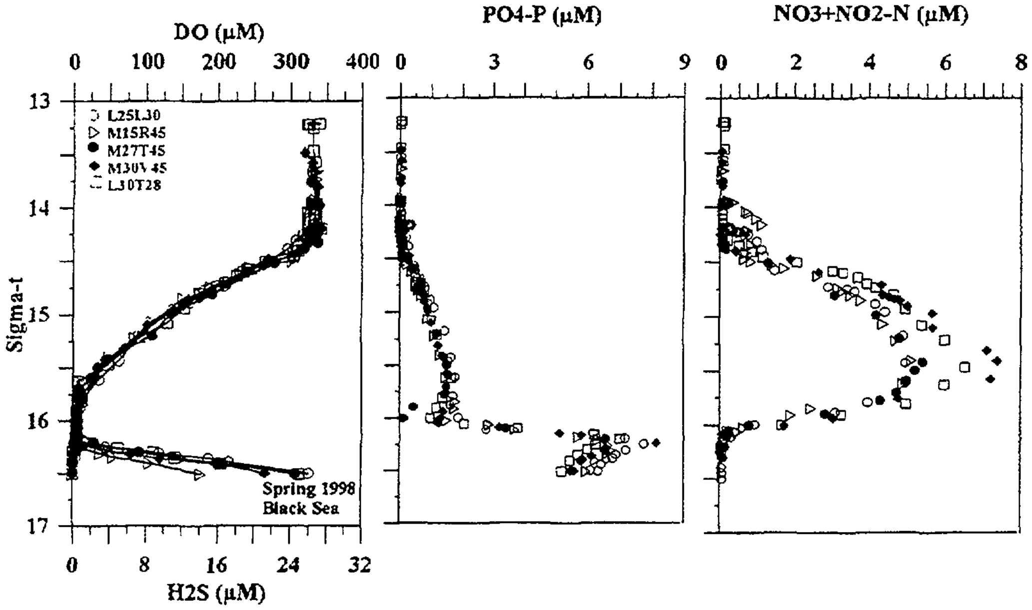

FIG 3 Vertical profiles of Dissolved Oxygen (DO)-H_2S and Dissoved Nutrients (PO_4-P a NO_3+NO_2-N) in the southern Black Sea for spring 1998 period

Primary Productivity and Related Parameters: The observed light penetration in the upper water column of the southern Black Sea during spring 1998 period indicated the thickness of the euphotic zone (defined as the depth of 1% of the surface light) to range between 25 and 35 m (Fig. 4). The less energetic, high wavelength component of the incoming light was absorbed in the upper surface layer (the top 10m), where the highest (downward) attenuation coefficient (K_d = 0.2-1.2 m^{-1}) was calculated. Below this layer the solar light penetrated with a constant K_d, which varied regionally between 0.1 and 0.3m^{-1}. The highest estimated K_d values were observed in the Rim Current region where the phytoplankton biomass and the photosynthetic production rates are relatively high.

Chl-a and in situ fluorescence data from different regions of the southern Black Sea are displayed in Fig.4. The concentrations in the euphotic zone were generally low (<0.5 µg/L) with the lowest values in the surface mixed layer, and a subsurface Chl-a maximum was formed near the base of the euphotic zone and below the seasonal thermocline or at a certain density surface σ_t = 14.25-14.5 having a concentration values up to 1.5 μg/L. In the central gyres where the upper boundary of nutricline is shallower, the subsurface maxima was fallowed by a sharp decrease while the chlorophyll-a profiles (as well as in situ fluorescence) have shown a secondary deep maximum in the Rim Current region. The deep secondary maxima were located at very low level of light (at 0.1-0.3 μE/m^2/s). In March 1998, chlorophyll-a showed almost uniform vertical distribution with 0.8 μg/L concentration.

Primary productivity profiles were similar throughout the southern Black Sea; the highest rates, which varied regionally between 1 and 5 mgC m^{-3} h^{-1} (or 10 and 50 mgC/m^3/d), were always determined in the upper euphotic zone down to the 10 % light intensity depth or the top 10-15m of the water column. Below this layer, the rate decreased markedly with depth and dropped to negligible rates at the 1% light intensity depth (Fig. 4)

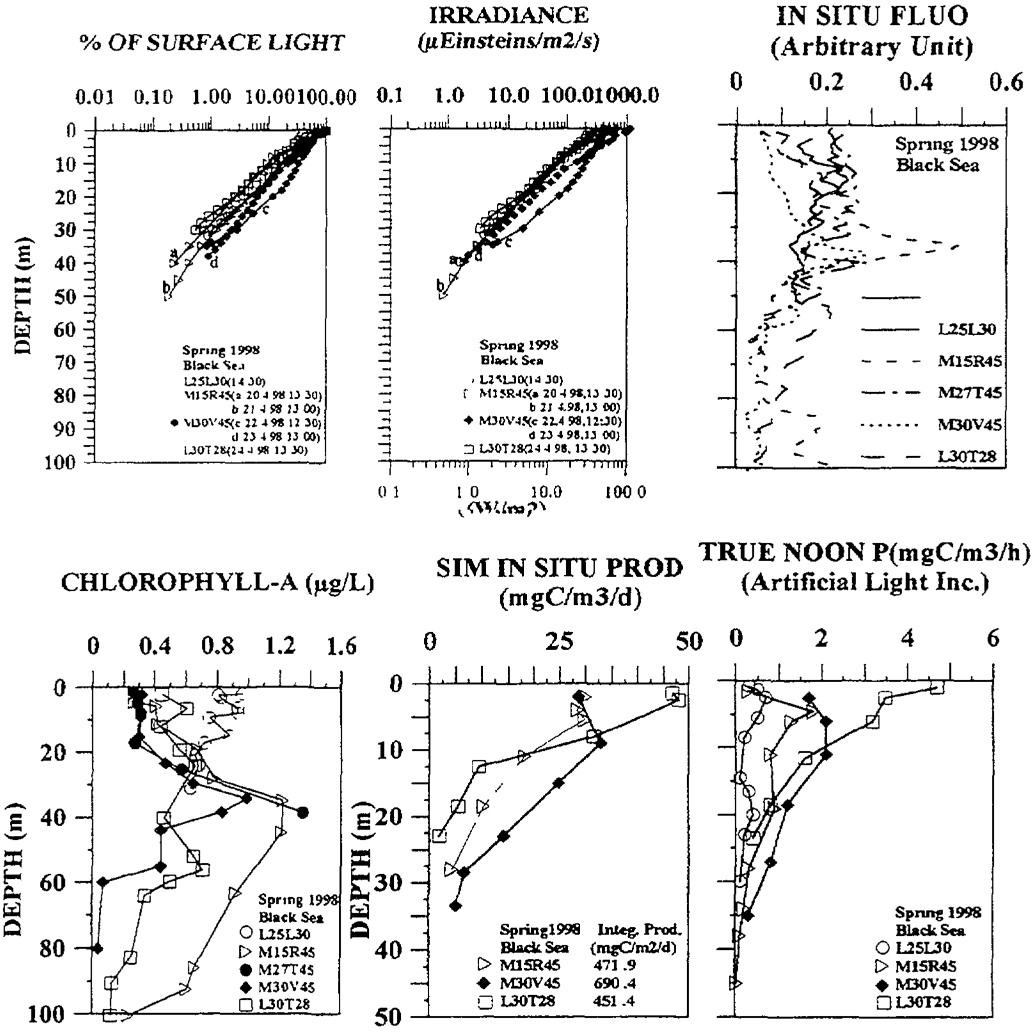

FIG 4. Vertical distribution of downward light in situ flourescence, chlorophyll-a and carbon production rates for Spring 1998 period

In order to determine the maximum rates of production, under adequate light intensity, samples taken from different depths of the euphotic zone were exposed to the full artificial light conditions in the incubator. The estimated maximum rates, were comparable with the surface values and the subsurface maxima of photosynthetic production rates coincided with the subsurface Chl-a maxima. The secondary but relatively weak peak of photosynthetic carbon production rates were observed at the same depths of deep secondary fluorescence maxima (as deep as 70-90m). The population living here was determined mostly as diatoms (E. Eker, unpublished data) and though the presence of very low level of light they were photosynthetically active. Such secondary maxima were

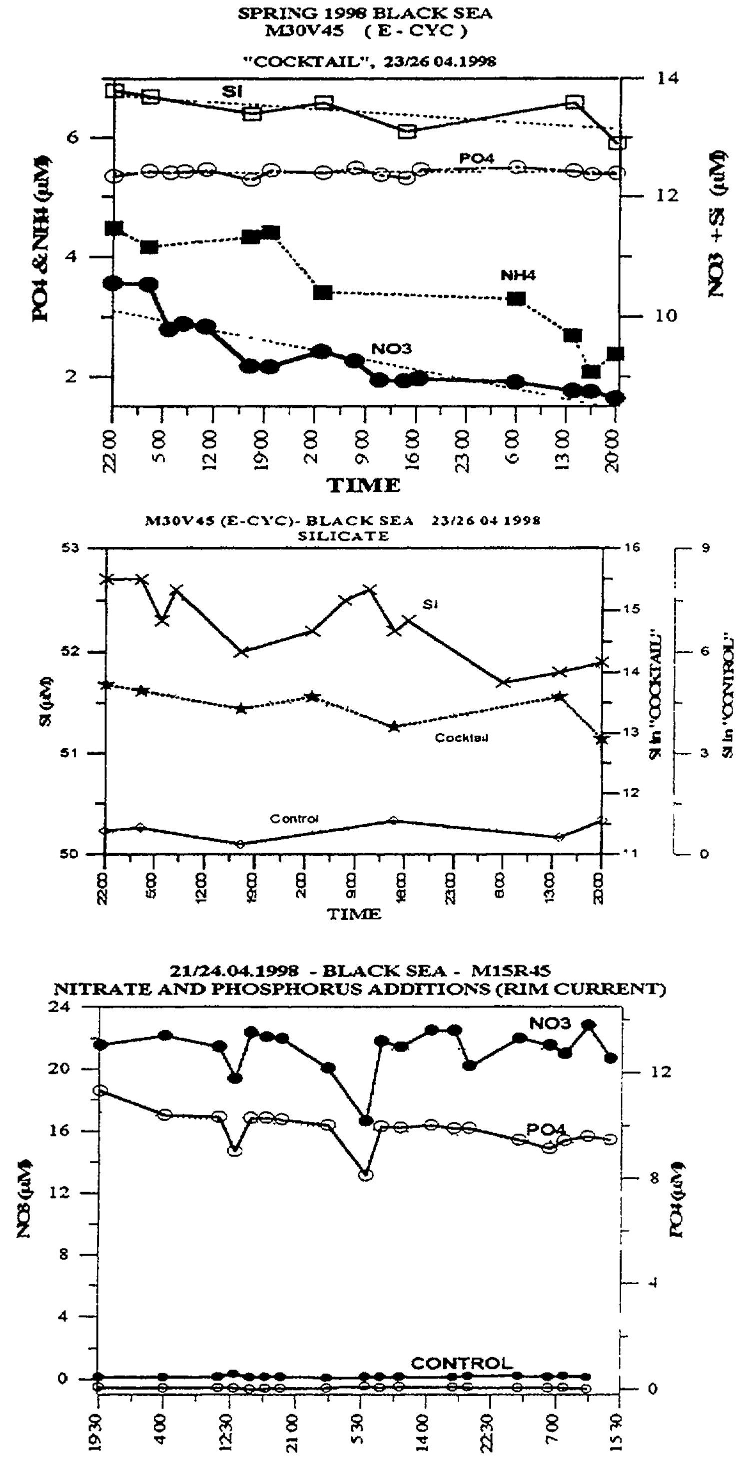

FIG. 5 .Bioassay experiments performed during Spring 1998 cruise

not observed in the central cyclones. The depth-integrated production rates ranged from 450 to 690 mgC/m^2/ d in the southern Black Sea for the late spring period while very low level of daily production (<50 mgC/m^2/d) was recorded in the Rim Current region in March 1998. The highest depth-integrated production rate was 0.7 gC/m^2/d in this region in Spring 1998 which is lower than the values already known for the NW shelf and off the Romanian coast for the 1970-1980 period [2] and very similar to those of the central Black Sea given for the late 1980 and early 1990s [17].

Bioassay experiments (using extra NO_3, NH_4, PO_4 and Si) performed during Spring 1998 cruise showed that under optimum light conditions the phytoplankton population is nitrate limited in the open waters. Phosphate seems to control the growth in the Rim Current regions of the southern Black Sea. Si concentration also influenced the phytoplankton growth since the majority of the population was determined as diatom (Fig. 5).

3. DISCUSSION

Coastal waters of the Black Sea are principally fed by the riverine input whereas the cyclonically dominated open ecosystem is mainly controlled by the influx of nutrients from the oxygenated lower layers by vertical diffusion and wind induced mixing processes that is much effective in winter. However, the input from the anoxic layer is limited due to the presence of a permanent halocline in the Black Sea. Halocline coincides with the suboxic zone where intense denitrification and redox-dependent processes also limit nitrogen and phosphorus input to the productive layer. In comparison, the role of atmospheric sources of nutrients appears to be marginal [28]. The f-ratio has therefore been estimated to be as low as 0.1 [13,22] and in such systems the f-ratio is mainly determined by the availability of ammonia [29].

As a result of as yet undefined processes, the upper CIL down to the temperature minimum depth in the Rim Current is enriched with nitrate but drastically poor in phosphate. There are thus very high N/P ratios in the upper nutricline and an apparent shift in the nutricline onset in the CIL. Since these P-limited CIL waters are mixed vertically with the surface waters in winter and early spring,bloom in such areas is limited by phosphorus. Nitrate-limited production occurs in the central gyres due the low N/P ratios of the chemocline established just below the euphotic zone. The relatively high atomic N/P ratios of POM indicate that the anomalously low ratio of nitrate/phosphate in the oxic/anoxic interface of the entire deep basin is due to nitrate removal via denitrification, greatly exceeding P-export from the suboxic waters [21].

On the other hand changes recently observed in the Black Sea such as the reduction in dissolved silicate load of Danube River by about two-thirds since dam constructions in the early 1970s, concominant decrease in witertime Si concentartion by more than 60% in the central areas [30], increase in nitrate concentrations in the NW shelf waters [4] and above the pycnocline in the whole Black Sea [13,14] significantly influenced the ecosystem of the lower trophic levels.

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IAEA-SM-354/31

IAEA-MEL's AQCS PROGRAMME FOR MARINE RADIOACTIVITY MEASUREMENTS

XA9951901

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Abstract

The main objectives of the IAEA-MEL's Analytical Quality Control Services (AQCS) for marine radioactivity measurements are discussed and future plans for the organization of intercomparison exercises and the production of certified reference materials are presented. The new developments should also include implementation of quality assurance programmes in Member States' laboratories, training in quality management and accreditation programmes.

1. INTRODUCTION

The IAEA-MEL has been assisting Member State laboratories in Analytical Quality Control Services (AQCS) for marine radioactivity measurements for almost 30 years (Fig. 1). AQCS through world-wide and regional intercomparison exercises and the provision of reference materials has been recognized as an important component of the IAEA's programme. Altogether 41 intercomparison exercises for radionuclides were organized and 35 reference materials produced.

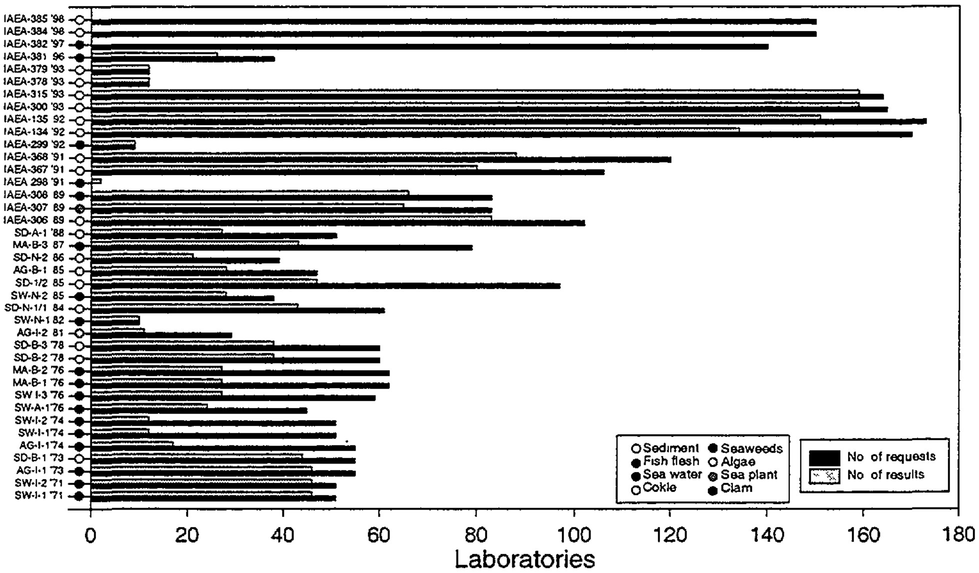

FIG 1. Intercomparison exercises carried out by IAEA-MEL for radionuclides

Following many years of experience in the AQCS programme and the recent recognition of the great importance of environmental data in economic, ecological and legal decision-making, the IAEA-MEL has been reviewing whether further steps should be taken to assist Member States in improving data quality. In particular, it has been proposed [1] that the AQCS programme should address in full the complex problem of the total quality management of analytical laboratories, including quality assurance programmes and manuals, regional and world-wide intercomparison exercises with proper feedback, production of certified reference materials according to ISO standards, training in quality assessment and control and accreditation of analytical laboratories.

The objectives of the AQCS programme carried out at IAEA-MEL to assist Member State laboratories in marine radioactivity measurements can be summarized as follows [1] :

i) To assist in quality assurance programmes through the organization of world-wide and regional intercomparison exercises.
ii) To provide feedback on the performance of the laboratories, to organize evaluation meetings, training and AQCS missions to improve their performance.
iii) To assist in the preparation of quality assurance programmes and manuals.
iv) To provide analytical reference methods.
v) To establish analytical competence and methods needed to produce certified reference materials according to ISO requirements.
vi) To provide reference materials and certified reference materials in sufficient types and quantities.
vii) To assist in accreditation programmes.

Further we shall discuss several concepts related to the full implementation of such a complex AQCS programme deriving background information from IAEA-MEL's experience obtained in recent years. All these activities would enable attainment and maintenance of the high standards and quality of the AQCS programme.

2. QUALITY ASSURANCE PROGRAMMES

Quality assurance (QA), as a system of activities and actions [2] to be taken to ensure confidence that analytical results will satisfy given quality requirements, has two components :

- quality assessment - a mechanism to verify that the system is operating within acceptable limits,
- quality control - a mechanism to control quality of data (to control errors).

The objectives of the QA programme include maintaining a continuous assessment and control of the quality of data, identifying proper analytical methods, providing permanent records of the performance of instruments, standardising analytical procedures, ensuring sample integrity, improving record-keeping and identifying training needs. The common aim of all these objectives is to provide data of high quality.

The QA functions include the development (or selection) of proper methods for sampling, sample preservation, sample pre-treatment, sample analysis and methods for evaluation and reporting of results. Further, they include intralaboratory and interlaboratory methods of validation and evaluation studies, establishing quality control guidelines and maintaining quality control sample programmes.

A laboratory without a proper QA programme cannot operate successfully. This is especially important when the laboratory produces series of data that are of interest in national or international programmes.

A QA programme (including good laboratory practices [3]) should be described in one of the most important laboratory documents - the QA manual. The document should contain the QA policy and objectives and should document the organisational structure of the laboratory, staff responsibilities, the analytical methods (including sampling, field measurements, sample handling, protocols, data reduction and evaluation), the materials and standards used, the QA procedures, interlaboratory comparisons, the recording system and the database. This comprehensive document should be regularly up-dated with any developments in the laboratory [4].

Therefore there is a need to assist Member States by establishing QA programmes in their laboratories, by providing them with examples of QA manuals, by training people in QA and by conducting AQCS missions.

As a typical example, we present in Fig. 2 the quality control chart (as drawn up in our laboratory) for analysis of ^{239,240}Pu in Irish Sea sediment (IAEA-135), which is frequently used as the

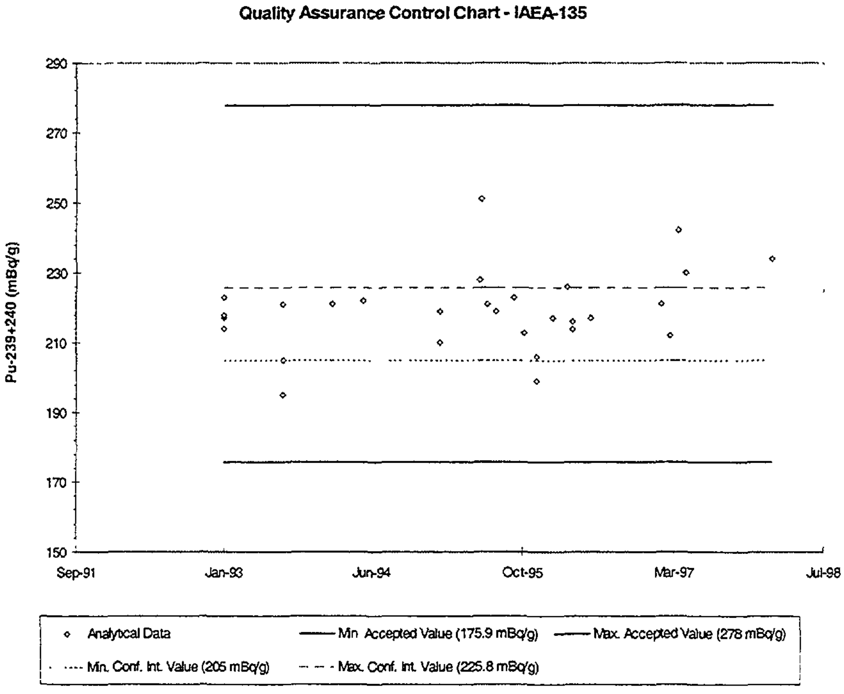

FIG. 2. Quality control chart of analysis of ^{239,240}Pu in Irish Sea sediment (IAEA-135)

reference material. The obtained data are mainly within a confidence interval of $\alpha = 0.05$, although a few exceptions were observed.

3. INTERCOMPARISON EXERCISES

Until now, both world-wide and regional intercomparison exercises have formed the main part of the AQCS programme [5]. They considerably helped Member State laboratories to assess their performance, supplied them with reference materials and enabled them to gather information on their performance. Although there has been remarkable growth both in the number of participating laboratories (from 40 to more than 150, see Fig. 1) and in the quality of data, we cannot yet be satisfied with the performance of all participating laboratories. As an example, Fig. 3 shows the performance of laboratories for $^{239+240}$Pu analysis in marine sediment from the Irish Sea (IAEA-135). It can be seen that there are about 20 laboratories performing very well in this intercomparison exercise (the total number was 151 and Pu results were reported by 48 laboratories). Usually the best results are for ^{137}Cs. Several laboratories have problems with analysis of other radionuclides e.g. ^{90}Sr, ^{241}Am, ^{210}Po, ^{210}Pb etc. Also, the geographical distribution of participating laboratories is very irregular (Western Europe - 90, Eastern Europe - 33, North America - 17, Central and South America - 13, Asia - 16, Australia - 6, Africa - 3, the Middle East - 2).

In a more recent intercomparison exercise on Arabian Sea sediment (IAEA-315) out of 159 laboratories, 52 reported ^{239,240}Pu results (Fig. 4). Although the ^{239,240}Pu concentration was lower by about a factor of three, the performance of laboratories was better than in the case of IAEA-135.

Following the ISO recommendation [6] in a recently completed intercomparison run with Irish Sea water (IAEA-381) z-score evaluation was introduced. Fig. 5 shows that for ^{137}Cs and ^{239,240}Pu, all participating laboratories have z-scores below 2, which indicates satisfactory performance (similar results were obtained for other radionuclides as well).

Several new marine samples for the next world-wide intercomparison exercises have been prepared, including Irish Sea fish (IAEA-382) Fangataufa lagoon sediment (IAEA-384), Irish Sea sediment (IAEA-385), Bikini Atoll sediment (IAEA-410) and Pacific Ocean sediment (IAEA-412).

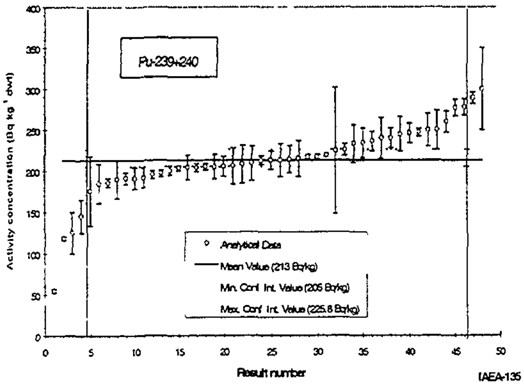

FIG 3. Data evaluation for $^{239\,240}$Pu in Irish Sea sediment (IAEA-135)

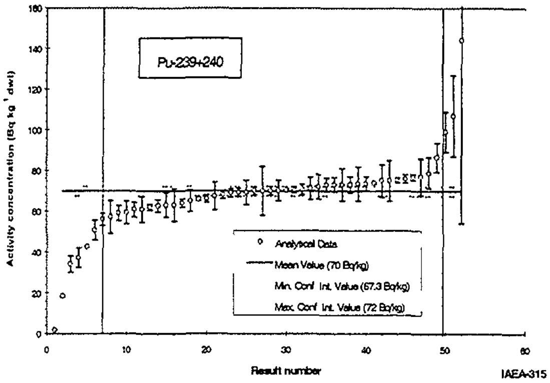

FIG 4. Data Evaluation for ^{239,240}Pu in Arabian Sea sediment (IAEA-315)

In order to improve the present situation in Member State laboratories it would be necessary to assist them with reference methods and protocols, to improve feedback from the intercomparison exercises by organising evaluation meetings to understand their analytical problems, to assist them with QA programmes and manuals and to organise QA oriented training and AQCS missions.

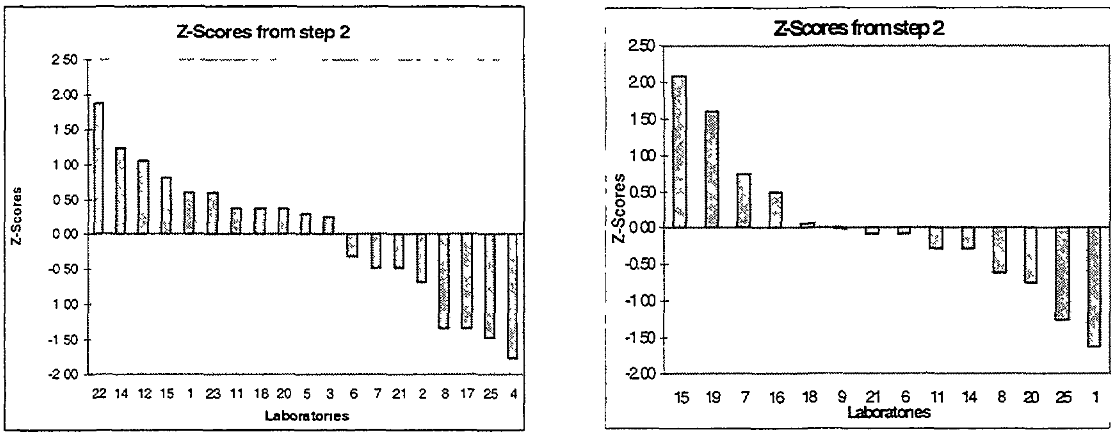

FIG. 5. Z-scores (left ^{137}Cs, right ^{239,240}Pu) of participating laboratories in the intercomparison exercise on Irish Sea water (IAEA-381).

4. REFERENCE METHODS

Reference methods [7, 8] represent a wide-ranging series of methods and guidelines used in marine radioactivity studies. Their format and terminology have recently been prescribed by the ISO [9], so they have a wide application throughout the world. They have considerable influence on the accuracy, precision and general reliability of data and represent a dynamic system based on current methods and new methods still under development. Periodic evaluation and modification of reference methods should keep the list up-dated with recent trends in analytical measurement techniques. Reference methods should be available for different sample matrices and elements. Their provision involves an extensive and time-consuming effort, including global cooperation and testing in expert laboratories.

5. REFERENCE MATERIALS

Reference materials (RM) represent samples of well established properties used for the assessment of analytical methods. More rigorous materials - certified reference materials (CRM) or standard reference materials (issued by the National Institute of Standards and Technology - NIST) have property values certified by technically valid procedures (at least with two independent methods) traceable to SI units [10].

RM and CRM have great impact on the development of methods of known accuracy. They represent important benchmarks in QA, identifying weak methodologies, detecting training needs, upgrading the quality of laboratories' performances and assessing the validity of analytical methods. The reference methods (or international standard methods) can only be accepted on the basis of interlaboratory tests performed on selected CRM.

The IAEA-MEL has until now produced RM as the final products of their world-wide intercomparison exercises. Regional exercises normally resulted in intercomparison samples with only recommended values. As RM and CRM represent high quality materials which usually cannot reasonably be used in everyday practice, laboratories produce their own secondary RM or working RM for frequent use in QA programmes.

With the aims of increasing the importance of the quality of data, of providing the required traceability to SI standards and of improving the accuracy and precision of Member State laboratories, the AQCS programme should also concentrate on the production of CRM. The CRM should be available for different environmental matrices e.g. sediment, water and biota.

The required long-term availability of CRM (over 10 years) necessitates their long-term stability and collection and preparation of large volume samples (over 100 kg). The relative precision of all reported data should be better than 5%. This would require highly homogenised samples thoroughly tested for any inhomogeneities of major elements (inhomogenieties should be below 2%). The principal analyses should be accompanied by supporting characterisation e.g. for multielemental composition, mineralogy, particle size distribution, radionuclide speciation studies etc. At least two independent analytical methods should be used for reporting certified values. This may not be a major problem in the case of radionuclides, where different methods are available (e.g. radiometric methods, ICPMS, TIMS, AMS, NAA etc.). Also, traceability to SI units seems to be more easily applicable to radionuclides than to elements and organic compounds. The interlaboratory testing should be based on expert laboratories only (10-20 laboratories).

Specific needs should be addressed for the production of CRM for mass spectrometric methods (e.g. AMS, ICPMS, TIMS) where usually small samples with very low radionuclide concentrations are necessary and require special treatment.

6. TRAINING

Training activities represent an important part of the complex AQCS programme. All three forms, i.e. long-term training in the Agency's or expert laboratories, training courses and expert missions to MS laboratories, can contribute significantly to the quality of data. However, more time should be devoted to all kinds of training in QA programmes. For example, the proposed calendar of IAEA-MEL training courses up to the year 2000 foresees, in some cases, up to 40% of time to be spent on QA programmes.

There is a general feeling that the Agency's support to developing Member States by supplying equipment in the framework of Technical Cooperation should be accompanied on a wider scale by the AQCS programme in order to create active laboratories producing reliable data.

7. ACCREDITATION

Laboratory accreditation, as a formal recognition by an independent research-based organisation that the laboratory is competent to perform specific analyses, has grown in importance in the last few years with the view to ensuring and maintaining high quality data. The accreditation process is beneficial both to the laboratories and to the users of their data. The objectives include the assurance of the validity of data, the acceptance of data without further tests, the credibility of laboratories, the promotion of good testing practices, the improvement of testing methods, the provision of technical information and the creation of competence.

The criteria for accreditation are very severe in order to maintain a high standard of analytical measurements. They include evaluation of the organisation, its staff, its facilities, the equipment, quality assurance, laboratory performance and protocols, quality of supplies, sample handling and recording system, the testing methods and procedures and the validation of performance and deficiency corrections.

To fully implement a complex AQCS programme in both the Agency's and MS laboratories, accreditation is the surest way forward. The Agency's laboratories should prepare for accreditation in accordance with the relevant ISO documents [5] and assist MS laboratories participating in the Agency's AQCS programme with their accreditation.

8. CONCLUSIONS

The Agency's AQCS programme, if taken in its complexity, can significantly improve the implementation of nuclear and non-nuclear analytical methods in MS laboratories. Data credibility is becoming essential in national and international programmes to which laboratories with different practices contribute. The AQCS programme should improve (a) the reliability of results from MS laboratories, (b) the comparability and compatibility of results and (c) their traceability to the SI system. The MS laboratories should benefit from regular participation in world-wide and regional intercomparison exercises, from intercomparison evaluation meetings, assistance in QA programmes and provision of QA manuals, supply of RM and CRM, analytical support from the Agency's laboratories (reference methods, AQCS missions) and long and short-term training. Recommendations to MS laboratories based on corrections to and improvements of their performance, evaluation of new ideas and developments in QA programmes, analytical methods and equipment, and finalisation of reference methods and protocols should considerably improve the quality of data.

The efforts of the AQCS programme should be directed towards international cooperation and coordination with active IAEA participation in standardisation activities.

New intra-Agency activities, like the development of internal QA programmes, reference methods, certified reference materials and development of the accreditation system, well harmonised in the different Agency units taking part in the AQCS programme, would considerably improve the Agency's output to the MS. The full implementation of the complex AQCS programme will, however, require new resources (manpower, budget) and wider cooperation with the Department of Technical Cooperation.

Acknowledgement

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ANALYTICAL QUALITY CONTROL FOR SPANISH ENVIRONMENTAL LABORATORIES USING THE ISO/IUPAC/AOAC PROTOCOL

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Abstract

The Spanish Nuclear Safety Council (CSN) organises in collaboration with CIEMAT periodical interlaboratory test comparisons for environmental radioactivity laboratories aiming to provide them with the necessary means to asses the quality of their results. This paper presents data from the most recent exercise which, for the first time, was evaluated following the procedure recommended in the ISO/IUPAC/AOAC Harmonised Protocol for the proficiency testing of analytical laboratories. The test sample was a Reference Material provided by the IAEA-AQCS, a lake sediment containing environmental levels of radionuclides: K-40, Ra-226, Ac-228, Cs-137, Sr-90, Pu-(239+240), whose reference values were established through the ALMERA intercomparison. The results of the proficiency test were computed for the 28 participating laboratories using the z-score approach, and the evaluation of the exercise showed that in 57 to 100 percent of cases, the analytical proficiency of the participating laboratories was acceptable, depending on the kind of radionuclide measured. The use of a z-score classification has demonstrated to provide laboratories with a more objective means of assessing and demonstrating the reliability of the data they are producing.

1. INTRODUCTION

There is a growing demand for environmental radioactivity measurements to be reliable, i.e. accurate and traceable to internationally recognised standards, and for their quality to be adequately demonstrated and documented. These requirements are particularly important when data sets generated by different laboratories are to be used to contribute to evaluation of data from environmental pollution research and monitoring programmes. World-wide acceptance of results from radiochemical analyses requires reliable, traceable and comparable measurements.

The Spanish Nuclear Safety Council (CSN) has the commitment to maintain high standards of quality in radioactivity measurements performed in national environmental laboratories. To this end it organises in collaboration with CIEMAT periodical interlaboratory test comparisons for Spanish environmental radioactivity laboratories aiming to provide laboratories with the necessary means to asses the quality of their results.

This paper presents data from the most recent exercise which, for the first time, was evaluated following the procedure recommended in the ISO/IUPAC/AOAC Harmonised Protocol for the proficiency testing of analytical laboratories(1). The test sample was a Reference Material provided by the IAEA-AQCS, a lake sediment containing the following radionuclides: K-40, Ra-226, Ac-228, Cs-137, Sr-90, Pu-(239+240). Originally there were only two radionuclides with certified reference values in this material:K-40 and Cs-137, but this list was subsequently extended to include Sr-90, Ra-226, Ac-228, and Pu-239+240, as a result of the ALMERA intercomparison(2) in 1997. The results of the proficiency test were computed for the 28 participating laboratories, and were supplied to the ALMERA data base. The evaluation of the exercise and the performance appraisal of each laboratory is presented in the paper.

2. DATA TREATMENT

The results provided by the laboratories were checked for consistency and a code was assigned to each analysing method, combining in the same code methods showing small differences. From the three independent determinations reported by each participant the mean was calculated, and the weighted mean when total uncertainty was informed. The statistical procedure applied for the analysis of results was the z-score, this method is the one recommended in the ISO/IUPAC/AOAC Protocol, in which the laboratory performance is assessed by using accepted statistics without any arbitrary scaling factors.

2.1 Establishing the assigned value

As mentioned, the test sample was already characterised in a previous intercomparison run (SL-2) , but only two reference values were derived (for Cs-137 and K-40). Within the ALMERA intercomparison most of the participating laboratories furnished six independent determinations which enabled comparison of individual laboratory variances with those of the whole data populations, providing a good evaluation of the reference values for further radionuclides. Data from the Spanish exercise were also supplied to the ALMERA data base. Table 1 shows the results of the intercomparison and their comparison with previous SL-2.

Once the reference values for the sediment sample were established, they were implemented in the Spanish scheme and the z-score treatment was applied. The final report of the Proficiency Testing⁽³⁾ with the evaluation of results was sent to the IAEA.

2.2 Formation of the z-score

The z-score was formed by comparing the bias estimate with a target value for standard deviation, as follows:

$$\mathbf{Z} = (x - \mathbf{X}) / \sigma \tag{1}$$

being x the weighted mean of the three independent determinations informed by each participant, **X** the ALMERA reference value for the activity concentration of each radionuclide (the "assigned value"), and their confidence intervals the target value for standard deviation (σ).

Since the frequency distribution of the scores (apart from outliers) was normal, the classification of proficiency data was established as:

$|z| \leq 2$ SATISFACTORY
$2 < |z| < 3$ ACCEPTABLE
$|z| \geq 3$ UNSATISFACTORY

The laboratory z-scores obtained in each analysis/nuclide were combined by using the following expressions:

RSZ : is the rescaled sum of z-scores obtained by a laboratory in an analytical system, and can be interpreted as standard normal deviates;

$$\mathbf{RSZ} = \Sigma \mathbf{z}_i / (\mathbf{m})^{1/2} \tag{2}$$

where **m**, is the number of scores being combined. The parameter was estimated in this exercise only for gamma spectrometry.

SSZ : is the sum of squared scores obtained by a laboratory in a round test, has a chi-squared (χ^2) distribution with **m** degrees of freedom for a well-behaved laboratory, and gives information on the magnitude of deviations

$$\mathbf{SSZ = \Sigma\ (z_i)^2} \tag{3}$$

TABLE I. ALMERA RESULTS AND COMPARISON WITH REFERENCE VALUES FOR PREVIOUS SL-2, REFERENCE DATE: 1996-01-01

	ALMERA (SED-1)					IAEA-(SL-2)				
Nuclide	N	O	B	Mean	RSD%	N	O	B	Mean	RSD%
				Man-made radionuclides						
				Bq/kg					Bq/kg	
Co-60	2	0	23	0.58	122	0				
Sr-90	22	10	2	1.13	18.6	5	2	1	1.24*	20.8
Sb-125	4	0	19	0.48	83	0				
I-129	3	1	4	0.041	47	0				
Cs-134	3	0	9	0.95	82	0				
Cs-137	38	2	3	1.99	14.1	15	2	1	1.88	15.2
Eu-154	3	0	16	-0.24	488	0				
				mBq/kg					mBq/kg	
I-129	3	1	4	0.041	47	0				
Pu-238	13	4	6	9.6	75	0				
Pu-239+240	20	5	2	71.2	9.9	3	1	0	44*	93
Am-241	12	6	11	27.8	5.1	0				
				Natural radionuclides						
				Bq/kg					Bq/kg	
K-40	41	4	0	239	8.9	18	2	0	240	18.5
Ra-226	21	0	0	18.5	17.0	16	0	0	22.9*	44.6
Ra-228	9	2	0	10.9	6.1	3	0	0	11.9*	1.0
Th-228	12	0	1	12.0	16.3	3	0	0	11.7*	5.5
U-238	9	2	1	14.5	13.2	3	0	0	15.0*	10.1

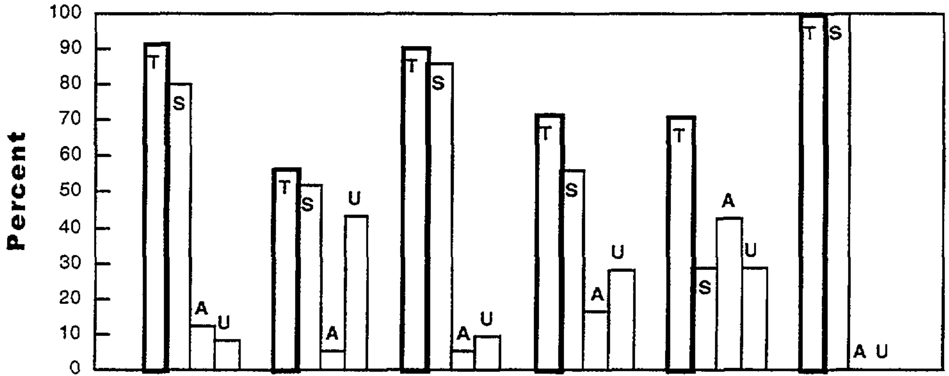
N - total number of laboratory means (without "less than" values)
O - number of results rejected by the test for outliers
B - number of "less than" values (not considered)
RSD - relative standard deviation for the population of accepted data (A=N-O)
* - not certified

3. RESULTS

The global results of the exercise are presented in Figure 1, where the percent of laboratories being classified as satisfactory, acceptable or unsatisfactory is displayed by radionuclide; the analytical proficiency has been found to be acceptable in 57 to 100 percent of cases. In the case of Pu-(239+240) the performance was hundred per cent satisfactory, but only 3 laboratories reported results. More detail can be seen in Figure 2 where the individual z-scores are displayed as bar charts for 3 representative evaluation cases:

- Ac-228 analyses were performed by all the laboratories by gamma spectrometry (G), and only two behaved unsatisfactory
- Ra-226 was determined by gamma spectrometry by 16 laboratories being classified as unsatisfactory the 31.25% , however from the 5 laboratories doing radiochemistry (R), 4 of them behaved unsatisfactory (80%)
- in the case of Sr-90, 3 different radiochemical techniques were employed for its determination: selective precipitation (PP), ionic exchange (II), and extraction-l-l (EX), being the best performance achieved by the PP technique.

Regarding the results of parameters **ssz** and **rsz**, a low percentage of laboratories performed the analyses with satisfactory analytical accuracy (22%). And the analytical bias in gamma spectrometry was found to be acceptable in 60 per cent of laboratories.



Nuclide	K-40	Ra-226	Ac-228	Cs-137	Sr-90	Pu-239/240
■ TOTAL (S+A)	92	57	91	72	71,4	100
☐ Satisfactory	80	52	86	56	28,6	100
☐ Acceptable	12	5	5	16	42,8	0
☐ Unsatisfactory	8	43	9	28	28,6	0

FIG. 1. Distribution percents of laboratories' performance by radionuclide in the exercise

4. CONCLUSIONS

The ISO/IUPAC/AOAC Protocol provides laboratories with a transparent and objective procedure of assessing and demonstrating the reliability of the data they are producing; the z-score treatment allows to set the performance criterion at the routine working level of laboratory participants.

The performance of the participant laboratories was good in general, although the estimated analytical accuracy was low. The best performance was achieved in measurements by gamma spectrometry (K-40, Ac-228 and Cs-137). Reported data for Pu-(239+240) analyses were all satisfactory, but the number of participants was very low. Major performance difficulties were found in radiochemical analyses for Ra-226 and Sr-90.

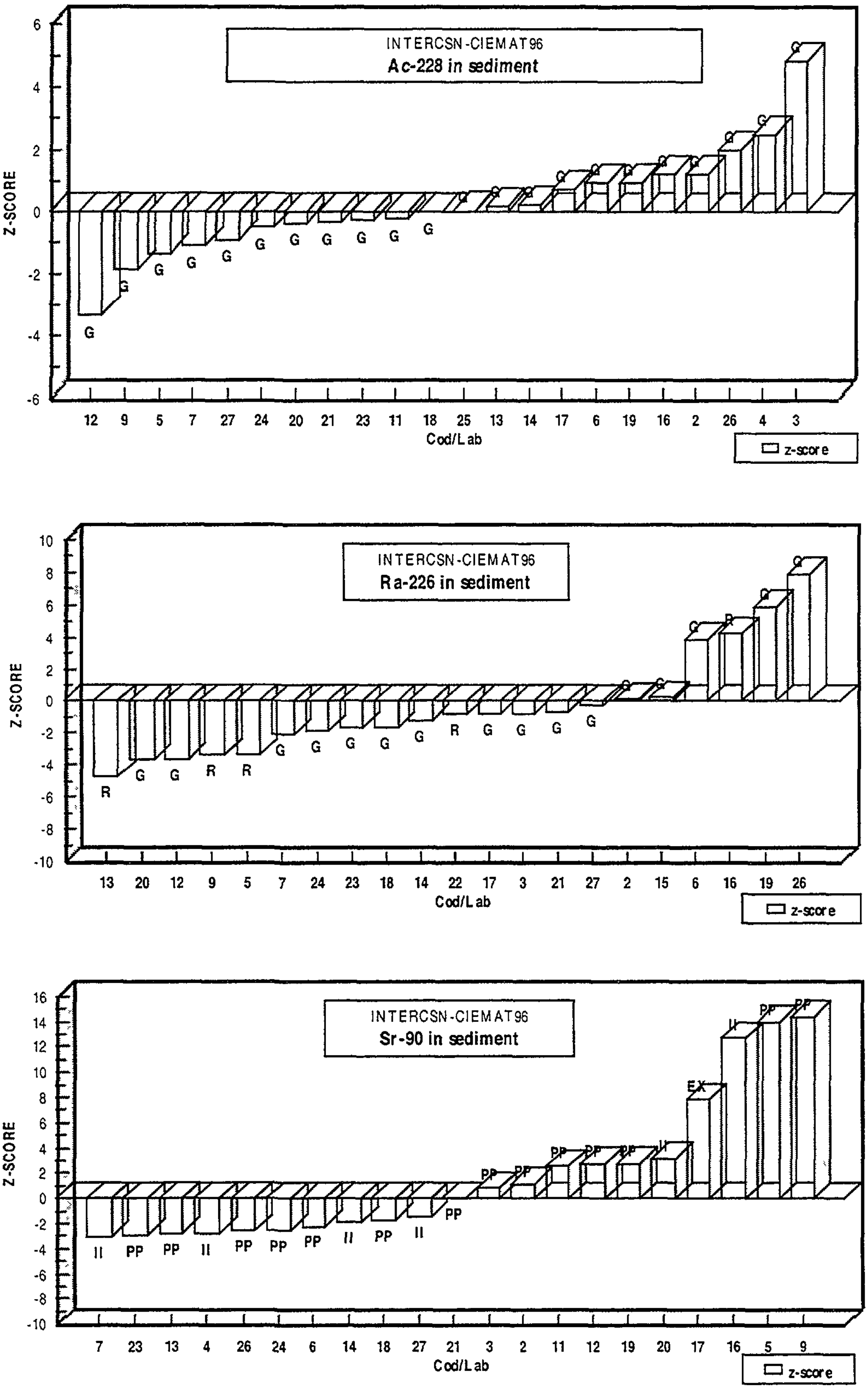


FIG. 2. Z-score for Ac-228, Ra-226 and Sr-90 analyses in sediment.

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FRESH BIOLOGICAL REFERENCE MATERIALS — USE IN INTER LABORATORY STUDIES AND AS CRMs

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Abstract

Biological reference materials were prepared and packed in tins and glass jars to be used in inter laboratory studies on chlorobiphenyls and organochlorine pesticides, and trace metals, respectively. The materials were homogenised, sterilised and packed as wet tissue, which is unique for the purpose of inter laboratory studies and offers the advantage of studying the extraction and destruction steps of the analytical methods. In addition to their use in inter laboratory studies, some materials have been prepared or are being prepared as certified reference material for chlorobiphenyl analysis.

1. INTRODUCTION

During the European project QUASIMEME (Quality Assurance of Information on Marine Environmental Monitoring in Europe) (Standards, Measurements and Testing Programme, SMT) from 1993-1996 five inter laboratory studies were organised both for trace organics (chlorobiphenyls (CBs) and organochlorine pesticides (OCPs)) and trace metals [1-3]. During the 3-years programme eleven materials were prepared, six for use in trace metal inter laboratory studies - three cod (*Gadus morhua*) livers, cod (*Gadus morhua*) muscle tissue, plaice (*Pleuronectes platessa*) muscle tissue and mussels (*Mytilus edulis*), and five materials for use in CB/OCP inter laboratory studies - two cod (*Gadus morhua*) livers, mackerel (*Scomber scombrus*) muscle tissue, plaice (*Pleuronectes platessa*) muscle tissue and mussels (*Mytilus edulis*). After 1996, when the QUASIMEME programme continues on a subscription basis, more materials were made.

The use of wet fish or shellfish tissue for inter laboratory studies on trace metal analysis was not known until now. The use of wet cod muscle tissue in an inter laboratory study on CBs was only reported once [4]. The obvious advantage of the use of wet fish or shellfish tissues in inter laboratory studies is that the participating laboratories are given the opportunity to demonstrate their ability of analysing CBs, OCPs and trace metals in a matrix which very closely resembles the matrices which have to be analysed in their routine monitoring work.

Until now for CBs and OCPs fish oils or fish fat were commonly used in inter laboratory studies [5-8]. Possible errors made in the extraction could obviously not be studies then. For trace metals freeze-dried or spray-dried materials have been used before [9-10]. These materials could show a different behaviour during destruction and their stability before or longer periods was not always guaranteed.

Because the stability of the wet materials made over a period of more than three years was good, a shellfish materials (mussels - *Mytilus edulis*) was prepared as a candidate certified reference material (CRM) for CB analysis.

2. MATERIALS AND METHODS

2.1 Preparation and packing of CB/OCP reference materials

All CB/OCP reference materials were thoroughly homogenised in a Stephan cutter. Attention was paid to avoid contact with any plastic materials to prevent contamination with plasticizers. The reference materials for CBs and OCPs were packed in tins. Two types of tins have been used. The mussels were packed in tins of ca. 80 g, height 55 mm and diameter 52 mm (Thomassen and Drijver, Deventer, The Netherlands). These tins, used for food preservation, are coated inside to prevent formation of rust. With regard to this rust formation the use of uncoated tins was considered too risky for the high-salinity mussel sample. Because the basic idea of using tins for the reference materials for CB and OCP determination was based upon avoiding all synthetic materials because of possible interferences during the analysis, these coated tins were subject to a blank test to check if any interferences could be transferred from the coating to the matrix. Two tests were carried out: 1) Extraction of the tin with 80 ml n-pentane, concentration of the n-pentane extract (20 to 1) and comparison with a blank of concentrated n-pentane that had not been in contact with a coated tin. This experiment was carried out to mimic the storage of a fatty tissue in a coated tin. 2) Extraction of the tin with 80 ml distilled water containing 30 g/L NaCl; extraction of the water with n-pentane and concentration of the pentane (20 to 1); comparison of this concentrated pentane extract with a blank concentrated pentane extract of distilled water. This experiment was carried out to mimic the storage of a watery matrix in a coated tin.

Fig. 1 shows that the first experiment caused a number of negative peaks in the GC/ECD chromatogram. This means that fatty tissue, particularly cod liver, will possibly extract interferences from the coating of the tin that may considerably disturb the GC/ECD chromatogram.

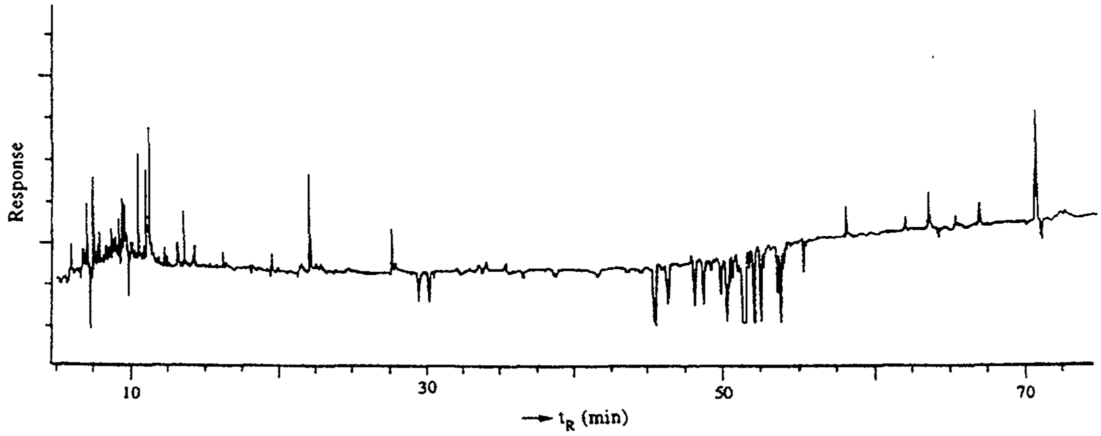

FIG. 1. Chromatogram of blank analysis of coated tin on a CP Sil 19CB column (exp.1) (Temperature programme: 3 min 90°C, 40°C/min to 215°C, 5°C/min to 270°C).

No significant differences between the test chromatogram and that of the blank were found in experiment 2. Considering the risk of rust formation when storing mussels in uncoated tins, these coated tins were selected for the storage of the mussel sample.

Uncoated tins are not used in the food industry. Therefore, they are not regularly available. A batch of uncoated tins was especially produced for this project by Carnaud Metal Box in France and delivered through Eurocan Food, Mechelen, Belgium. These tins were extracted with 80 ml n-pentane which was concentrated (20 to 1) and compared with a blank of concentrated pentane. This experiment was carried out in triplicate. No extra positive or negative peaks were present in the test extract in comparison with the blank pentane. These tins were consequently used for cod liver, mackerel and plaice.

In later experiments it appeared that the interferences shown in Fig. 1 do not pass conventional clean-up methods for CBs and OCPs such as alumina and silica columns. The materials packed in the uncoated tins showed a blackish layer inside after opening the after a few months or more. Although an effect of this blackish layer on the results of the inter laboratory studies was not seen, given the trapping of the interferences from the coatings during clean-up, it was considered to be safe to use coated tins also for more fatty samples.

The tins were filled to the brim (ca. 70 g) with the cold materials, directly from the Stephan cutter. Only cod liver was firstly transferred from the Stephan cutter to a round bottomed flask provided with a tap at the bottom and a stirring device. The cod liver was tapped from the flask during stirring, this to prevent separation of liquid and solid particles of the cod liver.

All tins were sealed by a Lanico TVM335 sealing machine (Thomassen and Drijver, Deventer, The Netherlands).

2.2 Separation and packing of trace metal reference materials

All trace metal reference materials were homogenised in a Stephan cutter. Initially some materials were packed in a plastic foil, a sterilisable laminate Steriflex PA, PE 30/100 (Sengewald, Germany). However, in spite of guarantees to be waterproof and fat resistant, a small sweating effect was found for lean materials stored at 37°C (ca. 1% decrease of moisture content after six months). In addition the lipid-rich (50%) cod liver caused leakages of the foils. The use of small glass jars, used in the food industry for packing caviar, appeared to be an acceptable alternative. These jars were equipped with twist-off lids. The inner part of these lids, which could come in contact with the reference materials, was provided with an epoxyphenol/eopxyphenyl lacquer, with a zinc carbonate content of less than 0.5 mg/kg. Although the producer guaranteed that the percentage of trace metals other than zinc in this lacquer was negligible, the jars were filled with distilled water, closed with the lid, shaken for 2 h and equilibrated for one day to test the possible presence of some trace metals. The contents of Hg, Cu and Zn were determined in the water. The contribution of the trace metal contamination to the concentration of the metals in the biological samples was less than 0.2% (Zn) which was considered acceptable.

The cod livers were, similarly to the CB/OCP cod liver materials, tapped from a round bottomed flask during stirring, while the other materials were taken directly from the cutter. Butylhydroxytoluene (0.02% w/w) was added to the cod liver as an antioxidant.

2.3 Sterilisation

The materials were sterilised in a 80 L Muvero-mat steriliser. The temperature was kept at 120°C for 30 minutes. The pressure was 2 bar. The total cooling time was 30 minutes. Because of the large quantity of samples, the temperature between the tins or plastic packages decreased somewhat slower than the water temperature. The effect of the slightly larger cooling time must, however, be regarded negligible. No irregularities were observed during the sterilisation process. A minimum stability of three years under moderate conditions is guaranteed for each of the materials.

2.4 Homogeneity tests

The homogeneity of the samples was initially tested by sodium and potassium determinations together with total lipid determinations according to Bligh and Dyer [11]. Later these determinations were replaced by determinations of some of the target compounds: CBs 118 and 153 for organic materials and zinc for trace metal materials. Each time 15 between-batch tests were carried out and 5 within-batch tests. The total number of lots in the batches was 200 for the tins and 300 for the glass jars.

F teste were carried out to identify a possible difference between the between- and within-batch test results. The contribution of inhomogeneity of the samples to the final result of inter laboratory studies was negligible. However, because during sterilisation some water or liquid lipids can separate from the bulk of the sample during sterilisation, the users of the materials are advised to rehomogenise the samples after opening and before taking the sub-sample for analysis.

2.5 Stability

An example of the stability of a CB material is given in Table 1. Given the persistent nature of CBs instability is unexpected and was not found indeed. Also for trace metals a good stability was found over a period of more than three years.

TABLE I. STABILITY: CBS IN MUSSELS 3 YEARS AFTER PREPARATION (CONCENTRATIONS IN μg/kg WET WEIGHT)

CB	t=0	Assigned value[1]	t=3 yr.
28	0.18	0.22	0.18
52	0.46	0.49	0.43
101	1.2	1.5	1.5
118	0.92	1.1	1.1
153	3.2	3.5	3.4
§38	1.8	2.2	2.2
180	0.38	0.39	0.41

[1] Assigned value from inter laboratory study in which the material was used.

3. RESULTS AND DISCUSSION

The fresh biological materials produced are suitable for use in inter laboratory studies on CBs and trace metals. The materials cover a wide range of concentrations (CBs: 0.1-400 μg/kg wet weight, metals: 0.02-40 mg/kg wet weight). The tins used are a suitable packing material for the CB/OCP materials. They offer a quantity of 70 g material to the participant of inter laboratory studies, which enables a sufficiently high sample intake in the case of lean samples. No disadvantages such as chromatographic interferences from the coating of the tins were observed during use. Fresh fish and shellfish samples to be used for trace metal analysis were successfully packed in glass jars.

It was possible to produce these samples with a very good degree of homogeneity. The contribution to the variance of the final results of an inter comparison exercise due to the inhomogeneity of most samples is less than 1%.

Because of the good homogeneity and stability of the materials made for inter laboratory studies, and because of the need for good quality CRMs, another European project was started under the SMT programme in which a candidate CRM, consisting of several thousands of tins with fresh, homogenised and sterilised mussels (*Mytilus edulis*), was prepared to be used for CB analysis. This material is currently being certified by fourteen expert laboratories.

Two other candidate CRMs will be prepared under the SMT programme in 1999: herring (*Clupea harengus*) for CBs and chub (*Squalius cephalus*) for non-ortho CBs.

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HISTORICAL LEVELS OF ^{99}Tc IN THE IRISH SEA

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Abstract

A 1 m sediment core, collected in 1986 from an accreting saltmarsh in the Solway Firth, was analysed for ^{99}Tc and the data used to assess (i) the accuracy of past discharge estimates and (ii) the behaviour of these past discharges in the Irish Sea environment. ^{99}Tc specific activities ranged from 1.6-19.3 Bq kg^{-1} dry with the maximum concentration appearing at a depth of 30-35 cm and a secondary peak (15.5 Bq kg^{-1} dry) at a depth of 70-75 cm. A chronology, based on both the current data and previous measurements of artificial radionuclides (^{137}Cs, ^{239,240}Pu and ^{241}Am) was applied to the core. The post 1978 ^{99}Tc concentration profile could be described by a simple model of on-shore movement of contaminated sediment from the Irish Sea and there is evidence to suggest that ^{99}Tc, like ^{137}Cs, has undergone redissolution from the contaminated sediment during periods of low discharge. Discrepancies between the model predictions and the ^{99}Tc concentrations observed prior to 1978 may result from the inadequacy of discharge estimates over this period, although diagenetic processes cannot be ruled out.

1. INTRODUCTION

The large increases in discharges of ^{99}Tc from the British Nuclear Fuels (BNFL) reprocessing plant at Sellafield, Cumbria, UK since 1994 have resulted in a renewed interest in the behaviour of this radionuclide in the marine environment. The currently accepted profile of ^{99}Tc discharges to the Irish Sea from Sellafield is illustrated in Fig. 1. Although ^{99}Tc is believed to have been discharged since operations began on site in 1952, the actual levels of discharge have only been accurately quantified since 1978. Discharges for 1952-1969 were estimated at 8 TBq year^{-1} by McColl *et al.* [1] using information provided by the BNFL Chapelcross Health and Safety Department. The discharge rate for 1970-77 was estimated at 40 TBq year^{-1} by Aarkrog *et al.* [2, 3] based on measurements of ^{99}Tc concentrations in seaweed from Arctic waters. There is, however, a great deal of uncertainty associated with these estimates. Aarkrog *et al.* [2, 3] suggest an error of at least 55%, while the McColl *et al.* publication [1] provides no details of the method of estimating discharges.

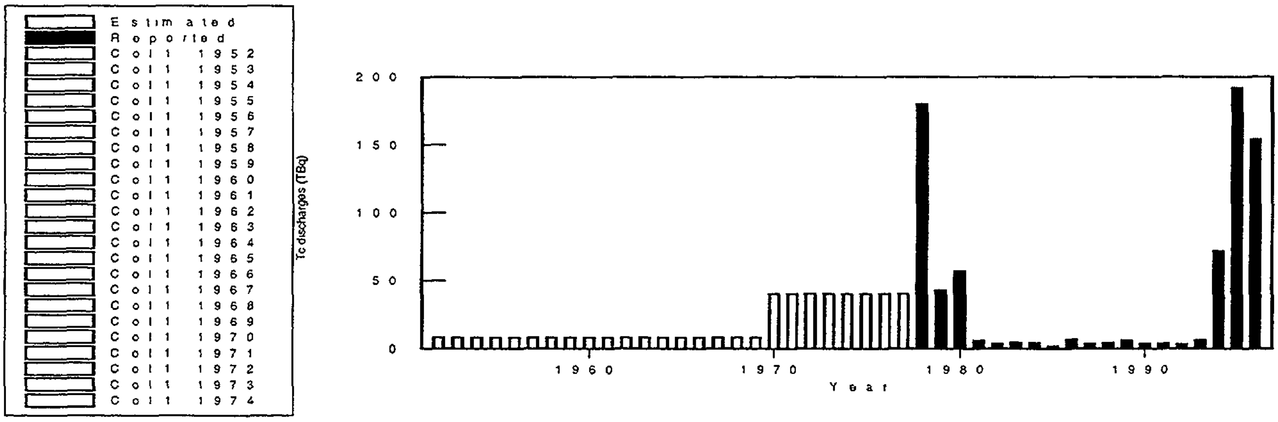

FIG 1. Annual discharge of ^{99}Tc from Sellafield

An alternative approach to reconstructing past discharges of ^{99}Tc from Sellafield was taken by Smith *et al.* [4]. They estimated the annual discharges in the period 1952-78 on the basis of the reported total beta discharges, assuming that the fraction of ^{99}Tc in these discharges was similar to that reported for the period 1978-81. It would seem unlikely, however, that this ratio would remain constant over this period. Both short and long-term changes in operational procedures at Sellafield will affect this ratio, especially since there is a large contribution from short-lived radionuclides (*e.g.* ^{106}Ru, half-life = 1 year) to the total beta discharge.

The lack of validated discharge data prior to 1978 is matched by a similar lack of information on the levels of ^{99}Tc in environmental materials collected from the Irish Sea in this period. Historical levels of other Sellafield derived radionuclides have been successfully reconstructed from the study of their concentration profiles in suitable sediment cores [5, 6]. In the present study, the ^{99}Tc levels in a sediment core collected from the Solway Firth have been determined and the results interpreted in terms of (i) the accuracy of past discharge estimates and (ii) the behaviour of these past discharges in this environment.

2. SAMPLING

A 1 m long sediment core was collected from a saltmarsh on the Solway Firth, south-west Scotland (Fig. 2) in March 1986.

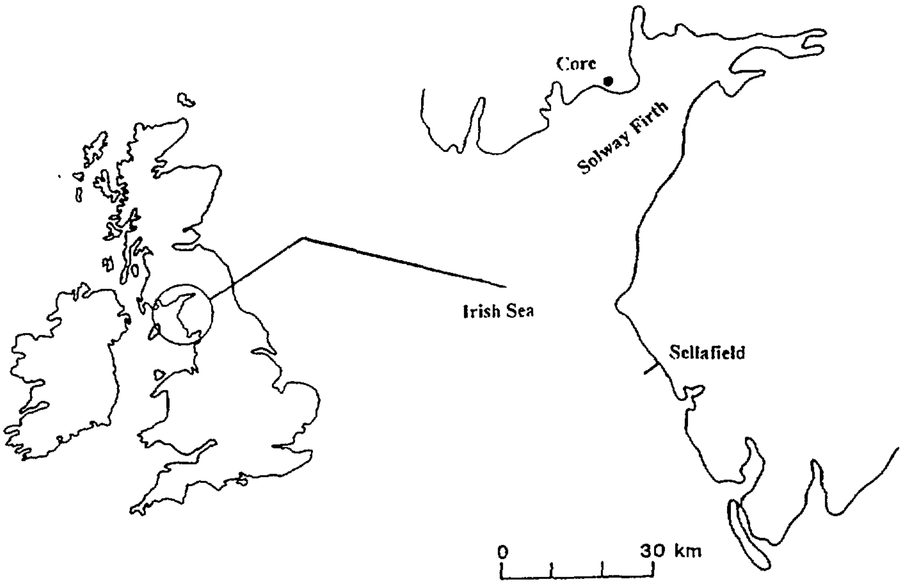

FIG 2. Sampling area

The core had been previously studied by MacKenzie *et al.* [6] and the concentration profiles of a wide range of radionuclides (including ^{137}Cs, ^{239,240}Pu and ^{241}Am) determined. From the results of that study it is known that this site experienced relatively rapid accretion with little post-depositional mixing, thus fulfilling the criteria required for the present study. The core was split into 2 cm (0-10 cm) and 5 cm (10-100 cm) sections and 20 g of sediment removed for analysis. The sediment was leached with 8 M HNO_3 and the isobaric interference of ^{99}Ru removed by the use of co-precipitation and chromatographic resins, using ^{95m}Tc as a chemical yield tracer. ^{99}Tc concentrations were determined by ICPMS using a VG Plasmaquad PQ2+ instrument. The concentration profile of ^{99}Tc is presented in Fig. 3.

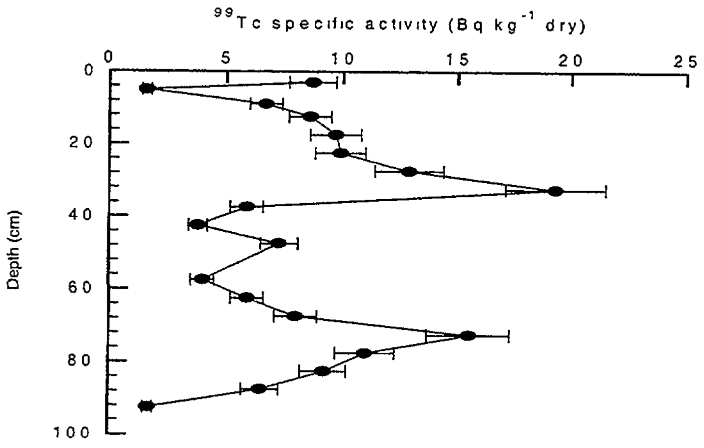

FIG 3 ^{99}Tc Concentration profile

3. DISCUSSION

^{99}Tc specific activities ranged from 1.6-19.3 Bq kg^{-1} dry with the maximum appearing at a depth of 30-35 cm and a secondary peak (15.5 Bq kg^{-1} dry) at a depth of 70-75 cm. If the dominant transport mechanism for ^{99}Tc from Sellafield to the Solway Coast was in solution then it would be expected that the concentration profile would closely mirror the annual discharge pattern. These two profiles have been plotted together in Fig. 4, with the assumption that the peak activity corresponds to the maximum discharge of 180 TBq in 1978. This assumption generates a deposition rate of 4.2 cm year^{-1}, slightly less than the value of 6.5 cm year^{-1} derived by MacKenzie *et al.* [6]. The latter value was based on a rather larger data set and is likely to be more representative of the average deposition rate throughout the entire core. It is not unreasonable, however, to assume that the rate of deposition may vary with depth and that the former value is more representative of the upper section. A composite chronology, assuming the lower deposition rate over the top 40 cm but an average deposition rate of 6.5 cm year^{-1} over the entire core has been utilised in this study.

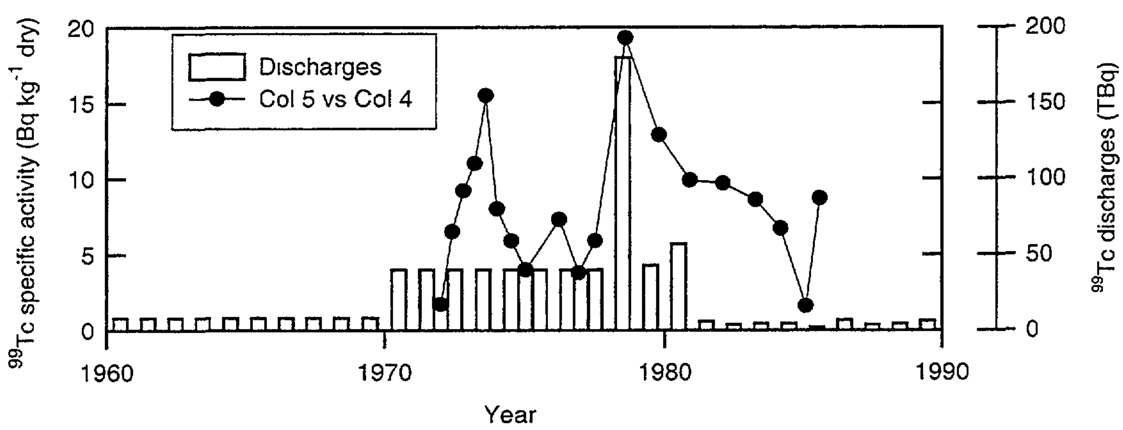

FIG. 4. Comparison of a ^{99}Tc concentration profile with the Sellafield discharge pattern

Given the uncertainty in the pre-1978 discharge data it is worth considering the post 1978 profiles in isolation. Although there is a qualitative agreement in the shape of the post 1978 profiles, the rate of decrease in the ^{99}Tc concentration (19.3 to 2-9 Bq kg^{-1} dry) is very small in comparison with the relatively large reduction in discharges (180 to 4-6 TBq) over the same period. A similar anomaly was found in this same core for the other artificial radionuclides studied by MacKenzie *et al.* [6]. The concentration profiles obtained for ^{137}Cs, ^{239,240}Pu and ^{241}Am could only be explained by assuming that on-shore movement of contaminated sediment from the surface of the Irish Sea was the dominant supply mechanism for artificial radionuclides to this site and a simple model quantifying the process was described [6].

This model assumes that in the pool of contaminated sediment supplying the material being deposited, there is an input of radionuclides controlled by the Sellafield discharge and a removal (a combination of radioactive decay, dispersion/dilution of the sediment and redissolution) which can be described by first-order kinetics. The system is described by the following equation:

$$dC_t / dt = I_t - \Lambda C_t$$

where C_t is the radionuclide concentration in the sediment pool at time t, I_t is the Sellafield discharge and Λ is the removal term. The removal term can be conveniently considered as a measure of the halving time (calculated as $\ln 2/\Lambda$) for reduction of the radionuclide concentrations. The effect of choosing different values for the half-time on the ^{99}Tc concentration profiles generated by the model are presented in Fig. 5.

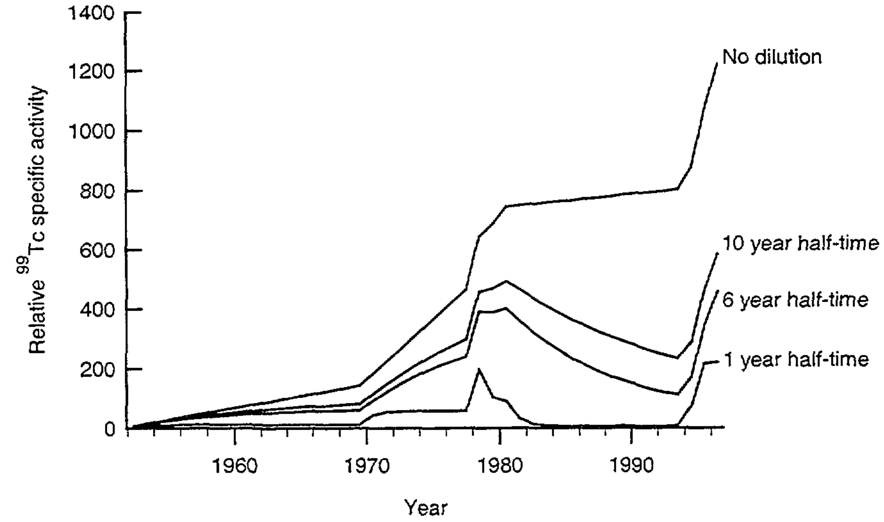

FIG. 5. ^{99}Tc concentration profiles generated by the model

For no dilution (*i.e.* an infinite half-time) the model predicts that the ^{99}Tc concentration in the pool of contaminated sediment and, hence, in the Solway Firth core, will continually increase.

As the half-time decreases, the ^{99}Tc concentration profiles generated increasingly resemble the annual discharge pattern. The best correlation between the model predictions and the ^{99}Tc concentration profile observed for the post 1978 period is obtained with a 3 year half-time (Fig. 6). The relatively good agreement over this period of known discharges, coupled with the ability of the model to explain the profiles observed for ^{137}Cs, ^{239,240}Pu and ^{241}Am, suggest that on-shore movement of contaminated sediment from the surface of the Irish Sea is the dominant transport mechanism for ^{99}Tc from Sellafield to this site. The relatively few historical measurements of ^{99}Tc in offshore sediments available suggest that the concentrations in this pool are suffice to cause the level of contamination observed in the Solway Firth. A core collected in 1982 had ^{99}Tc concentrations of between 11-50 Bq kg^{-1} dry in the top 30 cm [7], while two other cores collected in 1984/85 displayed a range of concentrations between 3-23 Bq kg^{-1} dry in the top 50 cm [8].

The half-time value assumed for ^{99}Tc (3 years) is similar to that derived for ^{137}Cs (3.5 years, with the effect of radioactive decay removed) but far less than that derived for ^{239,240}Pu (5.7 years) and ^{241}Am (6.6 years). MacKenzie *et al.* [6] concluded that the removal term for ^{137}Cs is greater because, in addition to dispersion/dilution of the sediment which is common to all of the radionuclides, it will include the effects of redissolution. It can be concluded, therefore, that ^{99}Tc, like ^{137}Cs, has undergone significant redissolution from the sediment in the contaminated pool during periods of low discharge.

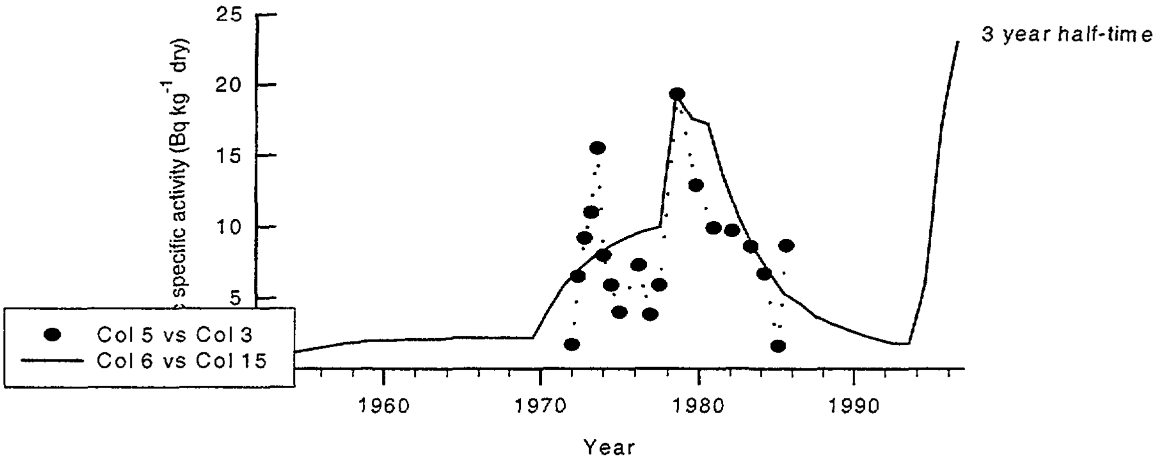

FIG. 6. Comparison of model prediction and ^{99}Tc concentration profile.

The rather poor agreement between the model predictions and core profile prior to 1978 may suggest that the currently accepted discharge history is flawed. In particular, the secondary peak at 70-75 cm would require an annual discharge in excess of 100 TBq year^{-1}. Complementary evidence is provided in a 1973 publication which reports that the ^{99}Tc concentration in *Fucus vesiculosus* collected from St Bees Head on the Cumbrian coast was approximately 18 kBq kg^{-1} fresh wt ("estimated from the discrepancy between γ-spectrometric and 'gross β' results, and other data") [9]. Regular monitoring of ^{99}Tc levels in *Fucus* has been carried out by the Ministry of Agriculture, Fisheries and Food (MAFF) since 1977 but it was not until 1995, when Sellafield discharged 190 TBq of ^{99}Tc, that such high concentrations were again observed. The year in which the original sample was collected is not actually stated and the method of determining the ^{99}Tc concentration was rather crude but nevertheless it does support the hypothesis that the magnitude of discharges prior to 1978 may have been episodically similar to current releases.

It could be argued, however, that the secondary peak at 70-75 cm may be an artefact of diagenetic processes within the sediment core. It has been postulated that under suitably reducing conditions ^{99}Tc, normally present in the environment as Tc(VII), could be reduced to the less mobile Tc(IV) state [10]. Although the redox conditions within this core have not been well characterised, reduction of Fe and Mn has been observed around this depth in other cores collected from this area [11].

4. CONCLUSIONS

The post 1978 ^{99}Tc concentration profile in the core can be described by a simple model of on-shore movement of contaminated sediment from the Irish Sea and there is evidence to suggest that ^{99}Tc, like ^{137}Cs, has undergone redissolution from the contaminated sediment during periods of low discharge. Discrepancies between the model predictions and the ^{99}Tc concentrations observed prior to 1978 may result from the inadequacy of discharge estimates over this period, although diagenetic processes cannot be ruled out.

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CADMIUM, LEAD AND ORGANIC MATTER DISTRIBUTION IN COASTAL SEDIMENT FROM THE ADRIATIC SEA

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Abstract

The spatial distribution of Cd, and Pb has been studied in surface sediments of the eastern Adriatic coastal region. In addition, Pb concentration has been determined in long sediment cores dating back to preindustrial time. The results indicate that trace metal concentrations in surface sediment layer depend both on pollution sources, and on local characteristics of the marine and terrestrial environment. Generally, most of the concentrations are not high revealing that the coastal area is not heavily polluted. Granulometric and geochemical data indicate the existence of some differences between sediments formed in the vicinity of fresh water input and sediments from areas without fresh water input.

1. INTRODUCTION

Coastal marine sediments are a major repository of trace metals as well as a major potential source of trace metals [1]. Man's activities (industry, agriculture, and traffic) affect the marine system, and in combination with mineralogical, morphological, granulometric and geologic characteristics of the sediment affect the chemical behaviour and distribution patterns of trace metal and organic matter in sediments. Organic matter is already known as a component of sediment directly related to trace metals distribution [2]. Behaviour of trace metals during estuarine mixing and in coastal marine sediments is largely related to their capacity for complexation with organic materials in truly dissolved, colloidal and macro-particulate phases [3]. The colloidal phase of trace metals from river and estuarine system can be removed from the water column such as small particles. Hence, the continental shelf alters the dissolved trace metals input from land into the open sea [3, 4].

2. STUDY AREA AND MATERIALS AND METHODS

Trace metals and organic matter were studied in sediments of the ecologically, economically and scientifically important eastern coastal area of the Adriatic Sea (Fig 1). The area is endangered due to untreated domestic and industrial waste discharges (stations 1, 6, 7, 8, 10 and 11) both, directly and via rivers (stations 2, 7 and 10) and streams draining storm water into the sea. Sediment samples were collected in July 1996 (Stations 1 – 5 and 7) and in July 1997 (Stations 6 – 11), using a plastic gravity corer of 6 and 3.5 cm internal diameter. The samples were frozen immediately after collection. Five centimetre long sediment samples from 11 stations were sliced horizontally into 1 cm long sections and analysed separately for Cd and Pb. In addition to this, lead and organic matter were analysed in much longer sediment cores sampled in July 1996 at stations 1-5 and 7 using a plastic gravity corer of 6 cm internal diameter. About 0,1 g of sediment sample (from each sediment layer) was digested using a mixture of acids in a Teflon vessel and heated [5]. The concentrations of lead and cadmium were measured using an atomic absorption spectrometer (Perkin-Elmer Model 1100 B, equipped with an HGA 700 graphite furnace and an AS 60/70 Autosampler System). A National

Bureau of Standards estuarine sediment (SD-M-2/TM) were treated and analysed for each trace metal in the same way as the sediment samples to evaluate the accuracy of measurement. The observed results showed great compliance with certified values: recovery was 93 % for Pb and 88 % for Cd.

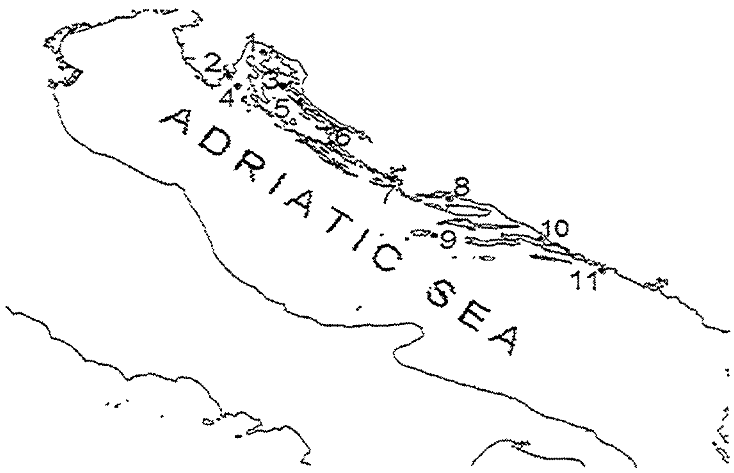

FIG 1. The study area with sampling sites

The organic matter content in the same sediment sections was determined by H_2O_2 treatment of samples at 450°C for 6 hours. The loss of weight after this treatment was assumed to be due to organic matter content [6]. Carbonate content was determined as weight loss after treatment with 4M HCl [8]. Granulometric composition was determined in 5 cm long sediment sections by sieving (>0.063 mm) and areometring (< 0.063 mm) according to Casagrande.

3. RESULTS

The content of fine fractions (< 0.032 mm) in sediment samples from all stations was relatively high and varied between 38-88 %, except from station 9, where it was only 16 % (Table 1). This station is located offshore while the others are located in channels, estuaries or near-shore areas. Organic matter is the principal component of fine-grained sediment.

The distribution patterns of Cd and Pb in the studied sediment samples revealed the existence of two zone having two different levels of trace metals. Figure. 2 shows that the Cd and Pb in general, are higher in sediment samples from the southern Adriatic, particularly from stations 7, 8 and 10 which are exposed to anthropogenic influences. The lowest concentration was found in the sediment sample taken from station 9. Station 9 is located far away from land based sources of pollution and the concentration is considered natural [8]. Station 11 is very specific. It is located close to the shore, but biological and chemical date indicate that it is under the strong influence of deep Adriatic water [9]. Cadmium concentrations were the highest at station 7 (0.487-0.747 mg/kg), located in the estuary of the river Krka. The estuary is used as a harbour for phosphate ore import and fertiliser export. On the riverbank the ferro-alloy factory was operated for more than 60 years, and raw material, products and by-products were drained directly into the estuary. The higher trace metal concentrations found in this area (three times as much as at station 9) may be related to the above mentioned activities. The discharge of untreated urban waste into the river estuary most likely also contributes to the increase in metal concentration. Organic matter content at this station is also high, 6.54 ± 1.48 %, while the sediment is of a fine-grained clayey silt type (Table 1). The main source of organic matter is the Krka river [10], but the contribution of urban wastewater generated by approx. 70,000 inhabitants, and discharged untreated into the estuary is a significant source as well.

Station 8 is located in front of the town of Split, the largest city on the Croatian coast. Urban wastewater discharged into the sea without treatment is the main source of organic matter. Organic mater content in the sediment sample is high, in the range between 5.7 and 7.2%. Station 10 is located in the area that is under the influence of the Neretva River and of the nearby town and harbour. The river drains runoff water from agricultural land. Concentrations of Cd and Pb and in the sediment sample from this station are high, while Pb is high in the sediment from station 11 (Fig. 2.).

TABLE I. GRANULOMETRIC COMPOSITION OF SEDIMENT FOR 5 CM. (SAND > 0.063 mm SILT 0.004-0.063 mm, CLAY < 0.004 mm) AND CARBONATE CONTENT (%).

Station	Sand (%)	Silt (%)	Clay (%)	Sed. type	< 0.032 mm (%)	Carbonate (%)
1	9	72	19	clayey silt	64	35
2	14	58	28	clayey silt	68	38
3	3	80	17	Silt	76	42
4	43	40	17	silty sand	41	39
5	42	48	10	sandy silt	38	57
6	16	63	21	clayey silt	62	41
7	14	62	24	clayey silt	63	55
8	8	62	30	clayey silt	80	45
9	78	15	7	Sand	16	73
10	1	68	31	clayey silt	87	39
11	3	51	46	clayey silt	88	21

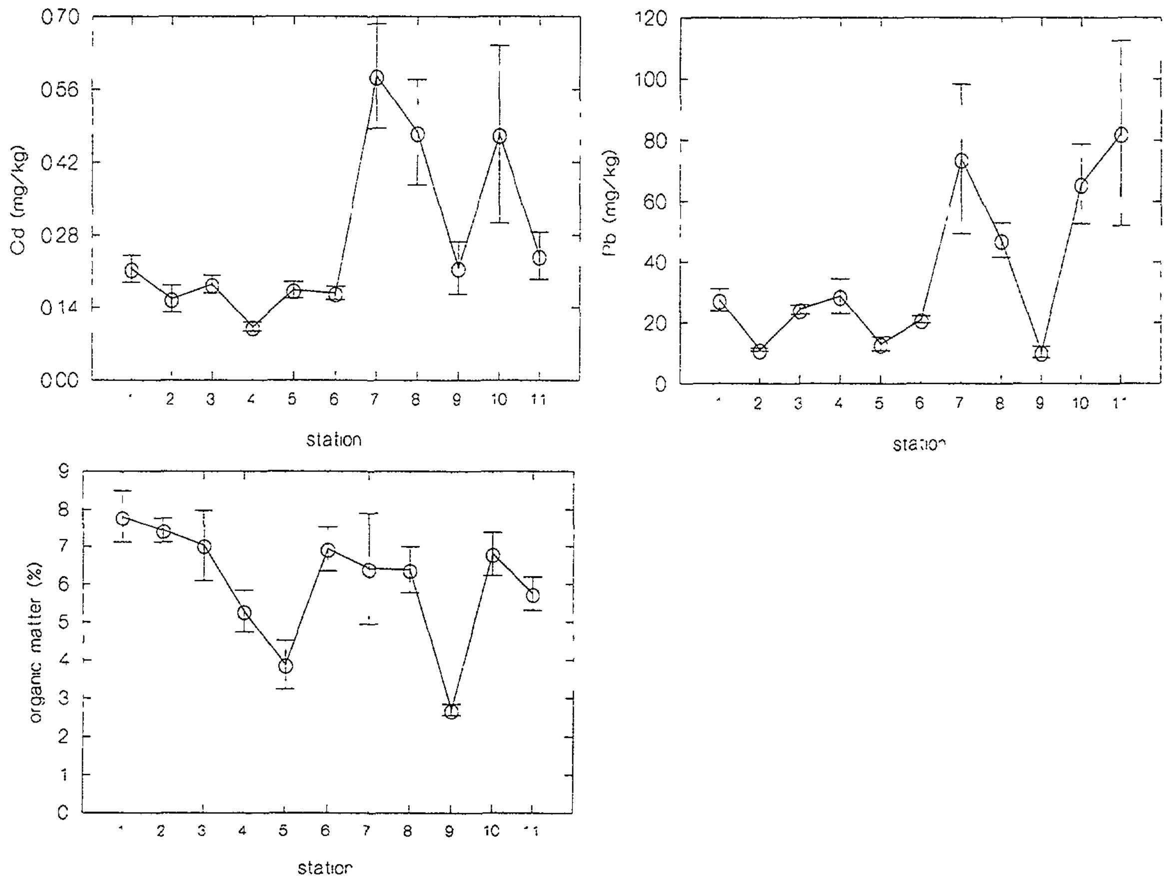

FIG. 2. Trace metal distribution and organic matter content in the sediment (upper 5cm) from 11 station from the coastal Adriatic Sea (Croatia).

The distribution pattern of organic matter differs from those for the trace metals (Fig. 2). While trace metal concentrations were much higher in the southern coastal area, particularly near industrial zones (stations 7, 8), the organic matter content in the most northern area is a little higher than in the other areas (Table 1). The high organic matter content may be related to the high input of suspended organic material from land based sources: rivers (stations 2, 7, 10) and urban waste outlets (stations 1, 8). The lowest content of organic matter was observed at stations 5 and 9, which are located far away from land based sources of organic matter. The sediment samples at these two stations are coarse- grained indicating the absence of organic matter, while at the other stations they are fine grained. Despite the fact that the organic matter content in sediment samples from stations 1-5 is high, the trace metal concentration at same stations are relatively low. This may be explained by the absence of a significant input of trace metals into the marine environment.

Figure 3 shows Pb concentrations in long sediment cores sampled at stations 1, 3 and 7. At stations 1 (nearby the town of Rijeka), 3 (island Rab) and 7 (Šibenik, the river Krka station) the increased Pb concentration in the 10 cm surface sediment layer may indicate an anthropogenic influence. The average Pb concentration in all samples was approx. 15 mg/kg, except at stations 1 and 7, where the average concentration was 22 mg/kg. The Pb concentration increase in the upper layers is not accompanied by an increase of organic matter content (Fig. 3). Organic matter content, in general, is higher in the upper part of the core. The average organic matter content in deeper layers is 5 %, while at the surface it reaches 8 %.

4. DISCUSSION

The coastal area, where the studied sediment samples were taken from, is very specific in terms of local oceanographic characteristics and due to fresh water influences. Sediment samples differ in their origin in prevailing sediment type and organic matter content as the result of the surrounding lithology, and local oceanographic characteristics. Sediment from station 3 and 4 are of biogenic origin, while stations 1, 2 and 5 are of terigenic origin. Cretaceous limestone and Eocene flysch are predominant in the entire coastal area, while alluvial sediments are rare, found mainly at river mouth (in the vicinity stations 2 and 10). In the non-polluted areas, the weathering process of land-based material is the main source of particles sinking on the seabed and forming marine sediments. Flysch is the main source of fine-grain clay particles, while coarse-grained sediment represents mainly preholocene and/or particles of recent marine biogenic origin. At stations that are not located in the immediate vicinity of the coast the predominant sediment types are silt (station 3), sandy silt (station 5), silty sand (station 4) or sand (station 9). Clayey silt type of sediment, with clay content between 19 and 46 %, is present at other stations. The highest content, found at station 11, is most likely caused by the discharge of fresh water from a nearby hydroelectric power plant, using the fresh water from the hinterland river Trebišnjica. It is confirmed by the lowest carbonate content (21 %), while at the other stations, the carbonate content varied between 35 and 73 % (Table I). The former indicates that the particles originated from a remote source area, are not primarily of carbonate composition, while the high carbonate contents at the other stations indicate the nearby origin of sediment particles. Organic matter contained in the marine sediment may be originated either from the sea or from the land (anthropogenic and/or natural source) [12]. The lowest organic matter content (2.6 %) was recorded at station 9, which is under the influence of open sea waters. Station 11 is also under the influence of open sea waters, but at this station the organic matter content is twice as high as at station 9. This is the consequence of the impact of the already mentioned nearby fresh water discharge. The highest values (6.3-7.8 %) was found in polluted bays and channels (stations 1, 6), in areas under freshwater influence (stations 2, 7, 8, 10) and indicate a land-based source of organic matter. By plotting the relation of organic matter with clay fraction content (Figure 4), stations can be separated into two groups; the first one containing stations that are not under the influence of freshwater, and the second one containing stations located in the vicinity of freshwater sources. The first group of stations, the organic matter content is linearly dependent on the clay particle content (r=0.923, P=0.009, b=2.049). The percentage of organic matter in the second group of station is lower than expected, which means that clay particles are primarily consisted of non-organic (mineral) matter, while at the first group the small size particles are of organic origin. Trace metals contained in marine sediments may be of natural and of anthropogenic origin. A question that should be answered is what is the natural background and what is the contribution of anthropogenic activities? Discharge of the trace metals either by rivers or directly into the sea would result in metal accumulation in marine sediments. In fresh and marine waters metals are adsorbing onto clay minerals and/or are bonding to organic matter. Flocculation and sedimentation of particle clay minerals trap organic matter, and trace metals remain trapped in the marine sediments. Primarily both high clay and moderate organic matter content may explain relatively high concentration of trace metals at station 11. Such high metal concentrations suggest that all metals are of anthropogenic origin collected over the very wide drainage area of the Trebišnjica River. The highest trace metal concentrations, recorded at station 7 are the result of the above mentioned sources of pollution, but they are also the result of specific local hydrodynamic characteristics of the Krka River estuary. Namely, a relative thick surface layer of fresh water is discharging through a narrow channel into the open sea, while the majority of marine water remains in the station area. Unexpectedly low concentrations of all trace metals were found at station 1, probably due to predominant current carrying discharged matter opposite to the station.

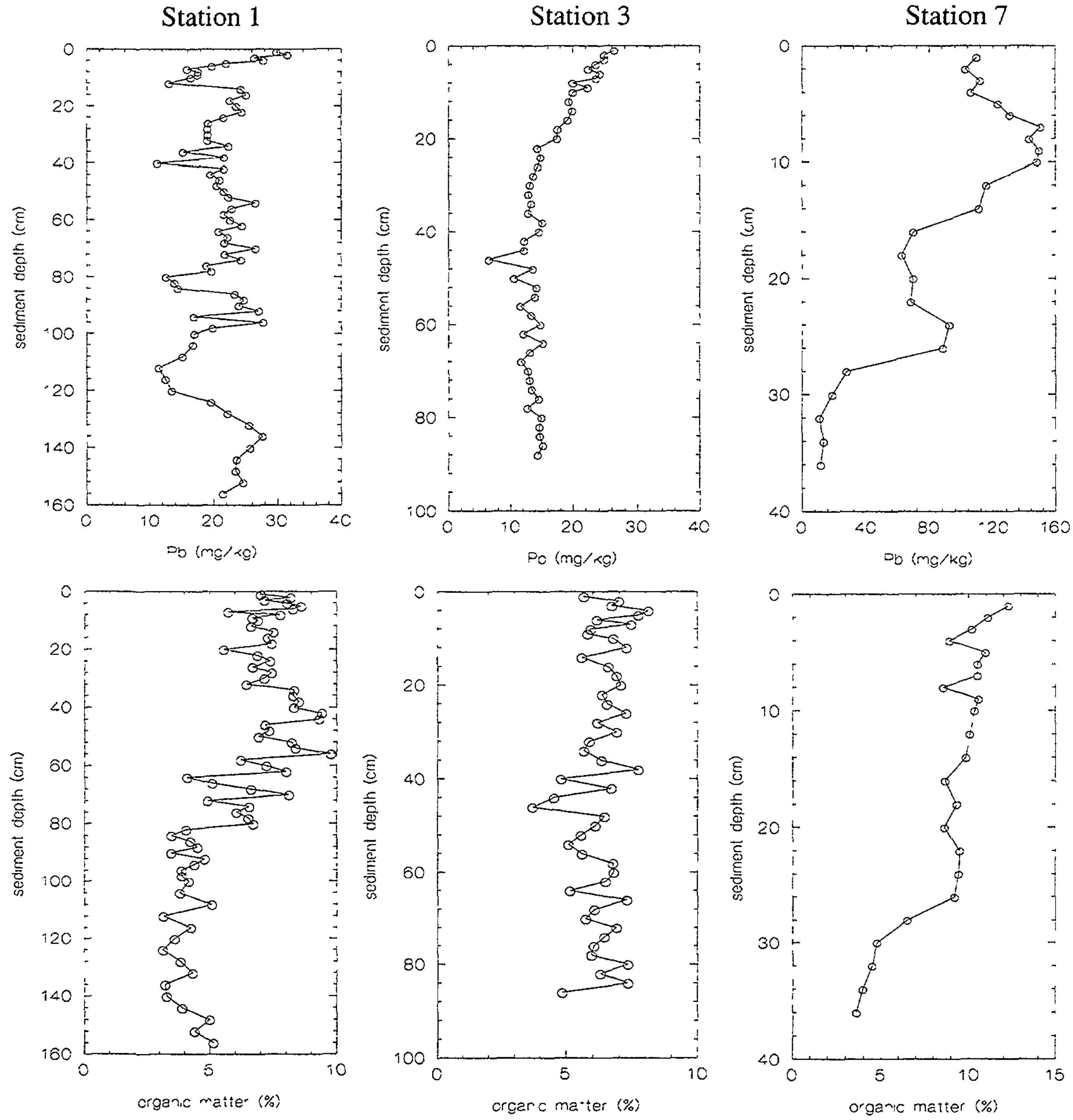

FIG. 3. Lead and organic matter distribution along the sediment cores from stations 1, 3 and 7.

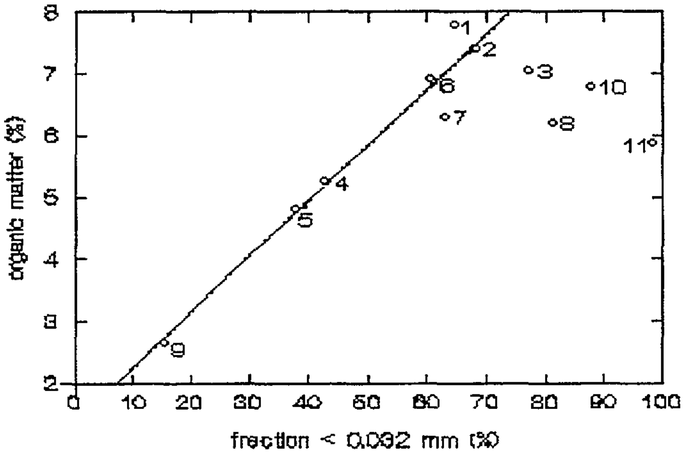

FIG. 4. Linear relationship between organic matter content and percentage of <0,032 mm sediment fraction.

Lead concentration in the long sediment core at station 1 clearly indicates the concentration increase in the top twelve centimetres (Fig.3). Taking the yearly estimated sedimentation rate of 1.7 mm [Juračić, unpublished data] this depth corresponds to the period of 70 years. Cs ^{137} measurements on the sediment sample indicated that the sedimentation rate is not higher than 3.2 mm/yr. [Barišić, unpublished data]. A similar concentration increases were found at station 3 where the sedimentation rate is higher due to river contribution; the concentration increase is visible in deeper layers similar as those at station 7. The background Pb concentration at station 1 is approximately 22 mg/kg, while at the two other stations the concentration is approximately 15 mg/kg, which is the result of the geochemistry of source material. The small decrease in the surface layer at station 7 is probably the result of a drastic reduction of all economic activities in the region that has occurred over the last 10 years. Variations in concentrations of Pb, particularly from stations very close to seashore, could be the consequence of temporal variations in precipitation and suspended matter input.

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ACCUMULATION OF HEAVY METALS IN SEDIMENTS OF MARINE ENVIRONMENTS ALONG THE SOUTHWEST COAST OF INDIA

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Abstract

In order to estimate the rate of excessive sediment accumulation that causes navigational problems and the impacts of urban and industrial development on sediment quality, concentrations of Cu, Ni, Zn, Cr, Mn, Fe and Ca, and radioactivity levels of ^{210}Pb and ^{137}Cs have been measured in nineteen sediment cores from estuarine, lagoonal, marsh, backwater and inner shelf areas along the southwest coast of India. Sediment accumulation rates in estuarine, lagoonal, marshy areas of the Karnataka coast (ELMKC) and Cochin Backwaters (CBw) are three to six times higher than those in the adjacent inner shelf areas, consistent with the deposition of terrigenous sediments in the river-sea interaction zones. Hydrogen sulphide was detected in most of the samples; sediment colour varied from shades of gray to dark green. Sediments have lower elemental concentrations and element enrichment factors (EFs) particularly for redox sensitive elements such as Mn due to prevalence of reducing conditions in the sedimentary column. Sediments of ELMKC and CBw have a predominantly terrigenous source. They contain low Ca contents, characteristic of tropical river sediments. In contrast, a higher Ca content of inner shelf sediments off both Karnataka State (ISKS-1) and Kerala State (ISKS-2) implies the importance of additional sediment ($CaCO_3$) flux from the marine biota. Measured Cu, Ni and Zn concentrations are generally low, perhaps reflecting the pristine nature of sediments. However, higher concentrations of Cr at all stations and of Zn at CBw indicate the input of Cr enriched minerals like amphibole and pyroxene from the catchment as well as Zn from anthropogenic sources. Heavy metal accumulation rates are high in estuarine, lagoonal, marsh and backwater areas along the southwest coast of India. This is not only due to the proximity of sources, but also due to high sediment accumulation rates because of the reduction of river flow in river-sea interaction zones owing to particle aggregation and sedimentation processes.

1. INTRODUCTION

The input of river suspended matter to the coastal ocean has increased in recent years due to soil erosion, deforestation and changes in the landuse patterns. It is estimated that 65% of the 24.8 billion tons of suspended sediment added annually by rivers to the oceans is from anthropogenic source [1]. Many tropical countries like India are plagued by problems of land erosion and of high particulate matter concentration in rivers. Heavy rainfall over the west coast of India (>2000 mm/yr) and the neighbouring Western Ghats (~5000 mm/yr) [2], and drastic reduction of river flow during river-sea interactions trigger the deposition of suspended matter in nearshore areas causing problems

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for navigation. Flooding is also frequent in the lower reaches of rivers during rainy season. Although the severity of pollution has not yet reached the levels noticed in industrialized countries, marine sediments near industrial sites and cities along the west coast of India show noticeable contamination [3].

Enrichment of heavy metals, radionuclides, radioactive pollutants as fission products, hydrocarbons, fecal coliform bacteria, sulphates, etc. is noticed in sediments around major cities like Bombay, Goa, Cochin and Trivandrum [3-6]. There are proposals to double the production and the number of industries at some places along the west coast of India by the year 2002. The eastern Arabian Sea is one of the most productive seas in the world. Fisheries is the major source of food for native people and also drives the economy. Fishermen face problems of siltation in estuaries and navigational channels and fall in fish catch in nearshore water due to contaminant input from the land. The decreas in living resource in nearshore waters along the west coast of India probably reflects the increase of contaminants like organochlorine pesticides, HCHs, DDTs, aldrin, dieldrin, endrin etc. [7]

The main objectives of this study are to estimate the sediment and metal accumulation rates using ^{210}Pb and ^{137}Cs isotopes and heavy metal data respectively. This investigation was taken up in view of sedimentation processes causing navigational problems due to deforestation and soil erosion in the west-flowing river drainage basins along the south west coast of India and the impact of urban and industrial development on sediment quality

1.1 The Study Area

The western continental shelf of India is one of the broadest in the world covering an area of 310,000 sq. km. The shelf is broad in the northern part (345 km off Bombay) and narrows down in the southern part (60 km off Cochin). The average shelf break occurs at 200m water depth. The inner shelf (<40-60 m water depth) is smooth, gentle, and blanketed by low carbonate, fine grained, organic-rich Holocene sediments. The outer shelf comprises of carbonate-rich sands of late Pleistocene age.

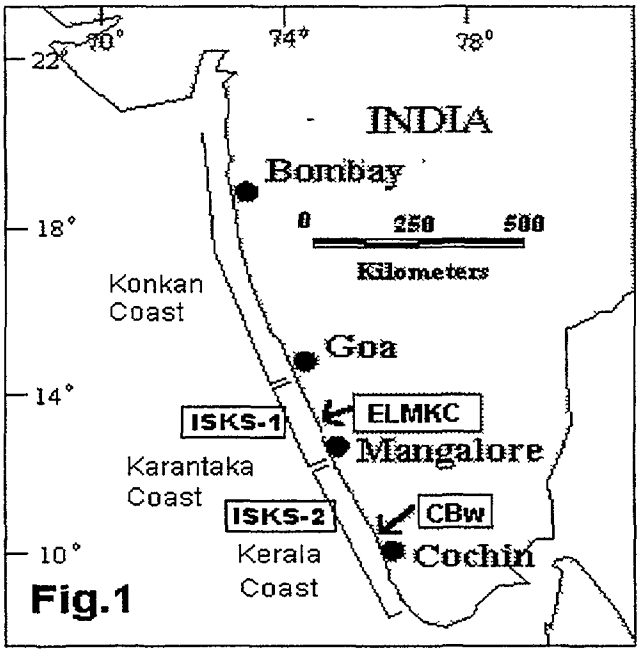

FIG. 1 The study area covers two southern states along the west coast of India which can be demarcated into: (i) Estuarine, lagoonal and marshy areas along the Karnataka coast (ELMKC), (ii) Inner shelf of Karnataka State (ISKS-1), (iii) Cochin Backwaters (CBw) and (iv) Inner shelf off Kerala State (ISKS-2).

2. MATERIALS AND METHODS

Nineteen sediment cores were collected from different marine environments along the southwest coast of India. Lead-210 was determined via its grand daughter ^{210}Po by alpha spectrometry, assuming secular equilibrium between them and negligible post-depositional migration in the sedimentary column [8]. Cesium-137 activities were measured by non-destructive gamma counting using hyper-pure germanium detectors [9].

The potential reactive metals like Cu, Zn, Cr, Mn and Fe, and Ca were measured in concentrated HNO_3 -leached samples by a Varian Spectra 250 AAS. Stream sediment reference materials (STSD 1 to 4) and duplicate samples were processed in a similar way to know the precision and accuracy of analysis. The errors of analysis are <4% for Cu and 6-12% for other elements. Sand content was measured by wet-sieving, and readily oxidizable organic matte in selected sample by Walkey-Black's method [10]. Carbon and nitrogen were measured in a few samples using a Perkin-Elmer CHN analyzer.

3. RESULTS AND DISCUSSION

3.1 Nature of sediments

The colour of sediment in all cores varied from shades of gray to dark green. Most of the sediment cores smelt of H_2S at the time of collection. Sand, partially/highly decayed vegetative matter and occasional gastropod and mollusc shells in deeper sediment layers are characteristic of estuarine, lagoonal and marshy sediments along the Karnataka coast (ELMKC). Due to the high sand percentage (20 - 93%), water and organic carbon contents are low (11 - 45%; 1.25 - 3.27%) in ELMKC sediment cores. In almost all the cores studied, sand content consistently increases downwards from surface indicating greater input of fine grained sediments from land in recent years Sediment cores from marshy areas have high vegetative matter, marshy plants, respiratory roots called pneumatophores and highly degraded calcareous shells suggesting severe reducing conditions that exist in deeper sedimentary layers. Carbon/nitrogen ratios are high (7.43-12.62) indicating the dominance of terrestrial organic matter.

In contrast to ELMKC, sediments from the inner shelf off Karnataka are fine grained (4 - 23%). Organic carbon was not measured in these sediments. However, the 2-3% organic carbon content at 20 m water depth does not much vary along the southwest coast of India [11]. Sediments from the Cochin Backwaters are relatively uniformly fine grained and rich in organic carbon (5.47 - 8.44%). Shells of macro-benthic organisms are rare. Organic carbon in Cochin Backwater sediments is 2-3 times higher when compared to that for inner shelf sediments off Kerala [11]. This is due to the discharge of effluents and organic wastes to the Backwater area [6]. As the sediment cores from the shelf off Kerala (ISKS-2) were collected from shallow depths (8-15 m) they contain a significant proportion of sand (2-64%) which is attributable to proximity to Pamba and Kallada rivers.

3.2 Sediment and heavy metal accumulation rates

The sediment accumulation rates along ELMKC range from 0.58 to 2.87 with an average of 1.21 ± 0.73 g cm^2 /yr (Table 1). As expected, the rates are high in estuaries of relatively large rivers when compared to smaller ones. The relatively large rivers in the study area are Kalinadi, Gangavalli, Sharavati, Gurpur and Netravati which annually discharge 6500, 5000, 9500, 2822 and 4600 million cubic meters of water and 0.48, 0.91, 0.27, and 0.44 million tons of suspended sediment to the coastal Arabian Sea [12-14]. The discharge from other small rivers is considered insignificant. Cesium-137 activity was measured in selected sub-samples. The average sedimentation rates deduced from the 1963 ^{137}Cs peak are in good agreement with the ^{210}Pb geochronology.

Sediment accumulation rate on the inner shelf (10-13 m water depth) off Karnataka is considerably lower (by 2.8 - 4.3 times) than the average estimated for ELMKC. This is due to the filtering of sediments in estuaries and adjacent wetlands which have contributed to a reduction in the

TABLE I. CONCENTRATION, ACCUMULATION AND ENRICHMENT FACTORS OF HEAVY METALS IN SEDIMENTS FROM VARIOUS MARINE ENVIRONMENTS ALONG THE SOUTHWEST COAST OF INDIA.

Parameters	ELMKC	ISKS -1	CBw	ISKS -2	R SPM[2]	G SPM[3]	Cont. Rocks[3]	Shale[4]
Sed. Rate[a]	1.21±0.73	0.38±0.1	2.77±1.33	0.46±0.24	-	-	-	-
Cu conc.[b]	51±18	29±1	91±33	22±2	71	100	32	45
accum.[d]	62±37	11±2.9	252±121	10±5	-	-	-	-
EF	0.75	0.7	0.99	0.45	1.14	-	-	-
Ni conc.[b]	54±19	50±1	67±3	43±3	173	90	49	68
accum.[d]	65±39	19±5	186±51	20±10	-	-	-	-
EF	0.53	0.8	0.67	0.57	1.84			
Zn conc.[b]	85±36	62±4	1496±314	65±5	90	250	127	95
accum.[d]	103±75	24±6.2	4144±1125	30±16	-	-	-	-
EF	0.6	0.71	10.7	0.63	-	-	-	-
Cr conc.[b]	212±112	125±22	172±8	155±7	-	100	71	90
accum.[d]	257±155	48±13	476±229	71±37	-	-	-	-
EF	1.58	1.51	1.3	1.6	-	-	-	-
Mn conc.[b]	242±124	447±194	472±205	186±10	724	1050	720	850
accum.[d]	293±177	170±45	1307±628	86±45	-	-	-	-
EF	0.19	0.57	0.38	0.2	0.62	-	-	-
Fe conc.[c]	7.01±2.34	4.33±0.17	6.9±0.3	5.07±0.36	6.5	4.8	3.59	4.7
accum.[e]	8.84±5.12	1.65±043	19±9.18	2.33±1.22	-	-	-	-
Ca conc.[c]	0.24±0.11	4.61±	0.57±0.37	4.68±0.81	0.26	2.15	4.5	1.6
accum.[e]	0.29±0.18	1.75±	1.58±0.76	2.15±1.12	-	-	-	-
EF	0.11	3.13	0.24	2.71	0.12	-	-	-

[a](g cm^2 /yr), [b](ppm), [c](%), [d](X10^{-6} g cm^2/yr) and [e](X10^{-3} g cm^2/yr).

width and draught of estuaries and navigational channels causing navigational problems and accumulation of land-transported contaminants.

For preliminary pollution assessment, elemental concentrations are compared with corresponding values for suspended particulate matter (SPM) from the study area [15], world river SPM (G SPM), average continental rocks [16] and shale [17]. Sediments of ELMKC have a predominantly terrigenous source and contain low Ca contents, a characteristic of tropical riverine sediments [15]. Manganese in ELMKC sediments is lower by factors of 2 to 4 when compared to that in continental rocks and shale, reflecting reducing conditions in the sedimentary column. The element enrichment factors (EFs; metal/Fe_{sample}/metal/Fe_{shale}) have been computed to infer anthropogenic accumulation of heavy metals. For most of the elements studied, the EFs are <1 with the exception of Cr suggesting that the sediments are not contaminated. The higher EF for Cr is due to Cr-enriched minerals like pyroxene and amphibole in the catchment material. In general, heavy metal accumulation rates are high in ELMKC than ISKS-1. This is not only due to proximity to the source but also to high sediment accumulation rates owing to particle aggregation processes like flocculation, agglutinization, biological uptake and fecal pelletization. The reduction of river flow due to river-sea interactions is the probable reason for high sediment accumulation rates along ELMKC. In ISKS-1 sediments, Cu, Ni, Zn, Cr and Fe are lower by factors of 1.1 to 1.7, but Mn and Ca are significantly higher by factors of 1.9 to 6 relative to ELMKC sediments. This suggests that the inner shelf sediments are relatively aerobic and receive carbonate flux from the marine biota.

In comparison with ELMKC, sediments of the Cochin Backwaters are relatively fine grained with sand content ranging from 3 to 66%. Sedimentation rate ranges from 2.67 to 3.20 with a mean of 2.77 ± 1.33 g cm^2 /yr. Probable reasons for high sediment accumulation rates are high river discharge, anthropogenic sediment input, development of harbours, dredging and the impact of sea-level rise. Among these, anthropogenic activities seem to be manipulating natural sedimentation processes in the backwaters. Periar and Muvattupuzha are important rivers and the former alone annually discharges 12,300 million cubic meters of water and 0.7 million tons of suspended sediment into the Backwaters [12, 13] .

The contents of Cu, Ni and Cr in sediments of CBw are relatively higher than those for average continental rocks and shale. However, EFs for these elements are <1. The higher concentration and EF of Zn indicate potential Zn contamination due to anthropogenic activities around Cochin, the second largest city along the west coast of India with a population exceeding one million and home to 70% of chemical industries of Kerala state [6]. The industries in and around Cochin are chemicals and fertilizers, insecticides, rare earths, petroleum products and aluminium and zinc or smelting. About 260 million cubic meters per day of partially treated or untreated effluents from these industries plus organic wastes, sewage and contaminants liberated by shipping activities in the Cochin port (established in 1936) are being added to the Backwaters. This eventually results in increase of contaminated heavy metals such as Zn, Cd, Pb, rare earths and radionuclides (Ra and Pb) in sediments [4, 18,19]

In contrast to CBw, sediment and metal accumulation rates are considerably lower in ISKS-2 (Table 1). As discussed earlier, terrigenous sediments are trapped in river-sea interaction zones which may explain this difference. The higher content and accumulation rate of Ca again reflect the contribution of Ca from marine biota.

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DETERMINATION OF ^{240}Pu/^{239}Pu ISOTOPE RATIOS IN KARA SEA AND NOVAYA ZEMLYA SEDIMENTS USING ACCELERATOR MASS SPECTROMETRY

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Abstract

Accelerator mass spectrometry (AMS) has been used to determine Pu activity concentrations and ^{240}Pu/^{239}Pu isotope ratios in sediments from the Kara Sea and radioactive waste dumping sites at Novaya Zemlya. Measured ^{239,240}Pu activities ranged from 0.06 - 9.8 Bq/kg dry weight, ^{240}Pu/^{239}Pu atom ratios ranged from 0.13 to 0.28, and ^{238}Pu/^{239,240}Pu activity ratios from 0.02 to 0.6. Perturbations from global fallout isotope ratios were evident at three sites: the Yenisey Estuary and Abrosimov Fjords where ^{240}Pu/^{239}Pu ratios were lower (0.13–0.14); and Stepovogo Fjord sediments where ratios were higher (up to 0.28) than fallout ratios. Based on procedural blanks, detection limits for AMS were below 1 fg Pu and the method showed good precision for isotope ratio measurements, minimal matrix, interference and memory effects. For high level samples, comparison between alpha spectrometry and AMS gave good agreement for measurement of ^{239,240}Pu activity concentrations.

1. INTRODUCTION

The total input of plutonium to the Arctic is dominated by global fallout from weapons testing [1-3]. However, additional plutonium sources include dumping of radioactive waste [4], marine and terrestrial transport from reprocessing plants [5], Novaya Zemlya weapons tests [6], and accidents such as the B52 bomber crash at Thule and the sunken nuclear submarine Komsomolets [Table 1]. Regional sources can often result in localised contamination and perturbations from global fallout levels. This is exemplified by the high Pu concentrations documented at Thule [12,13], the Chernaya Bay [6], the Kara Gate [2] and radioactive waste dumping sites at Novaya Zemlya [9,14].

Different sources often exhibit characteristic Pu isotope ratios. Hence, these ratios can be used to identify the origin of contamination, calculate inventories, or follow the migration of contaminated sediments and waters. Joint Norwegian Russian Collaborations (JNRC) demonstrated that the general level of radionuclides at Novaya Zemlya dumping sites was similar to the Kara Sea. However, at certain sites, enhanced levels of ^{137}Cs, ^{60}Co, ^{90}Sr and ^{239,240}Pu in sediments indicated that leakage from dumped objects had occurred [9,14]. Although some ^{238}Pu/^{239,240}Pu data are available on the JRNC samples [9,15], no investigation of the ^{240}Pu/^{239}Pu ratios had been carried out. With this in mind, the objective of the present study was to obtain further information on the Pu-isotopic signature in these sediments and to gain better insight into the source of the excess plutonium. Plutonium-240/239 ratios were determined using accelerator mass spectrometry, which has proved to be a useful and reliable method for analysis of Pu-isotopes.

2. EXPERIMENTAL METHODS

2.1. Sample preparation

Samples for AMS measurement represent a total of six sites: the Open Kara Sea; the Kara Gate (SW of the Kara Gate, South of Chernaya Bay); the Abrosimov and Stepovogo Fjords at Novaya Zemlya; and the mouths of the Ob and Yenisey Estuaries [Table 2]. Kara Sea and Novaya Zemlya sediment samples were collected during joint Norwegian-Russian expeditions to dumping sites during

1992, 1993 and 1994 [2,9,14]. The two surface sediment samples from the Ob and Yenisey Estuaries were collected during the Norwegian-Russian Karex expedition in 1994; the 1996 La Hague effluent sample (Joint Norwegian-French Collaborations) was included for comparative purposes.

Dried, ground and homogenised aliquots sediments (5–10 g) were ashed and/or digested with aqua regia, filtered and the extract taken to dryness. Pu-isotopes were separated by anion exchange chromatography using ^{242}Pu as a yield monitor. A few samples were also prepared by leaching electrodepoisted Pu-isotopes from stainless steel planchettes used for alpha spectrometry. After addition of Fe-nitrate, the samples were ashed to give final preparates for AMS measurement as Fe_2O_3 (2 mg Fe), with ^{242}Pu:Fe iron atom ratios of between 10^{-10} and 10^{-9} by design. All sample preparation was carried out in clean, low-level or trace element analytical laboratories.

2.2. Accelerator Mass Spectrometry

AMS measurements were carried out using the 14UD tandem accelerator at the Australian National University, Canberra; full details of the analytical technique have been reported elsewhere [16]. The Fe_2O_3 samples were mixed with Al powder, pressed into Al holders and mounted on a sample wheel. PuO^- ions from the negative ion source were injected into the 14UD accelerator and accelerated to 4.3 MeV. At this energy, electrons were stripped from the ions in a low pressure gas to dissociate the molecular ions and produce multiply-charged positive Pu-ions. After further acceleration, $^{A}Pu^{6+}$ ions were selected by an analysing magnet and counted individually using a longitudinal-field ionisation detector. This detector has an energy resolution of about 3 % for 30 MeV Pu ions, which is sufficient to resolve Pu^{6+} ions from other ions of the same magnetic rigidity but lower charge states. The three Pu-isotopes (mass 242, 240 and 239) were counted sequentially using repeat cycles for each sample. The accelerator and beam transport system were optimised using a mixed thorium oxide/iron oxide sample, and inflection magnet and terminal voltage settings for each of the plutonium isotopes extrapolated from the ^{232}Th values. Mass calibration was carried out against a certified Pu-isotope ratio reference standard (UK Certified Reference Material No: Pu 5/92138).

TABLE 1: ESTIMATES OF HISTORICAL AND POTENTIAL SOURCES OF PLUTONIUM TO ARCTIC AREAS. TOTAL RELEASES AND ESTIMATED INPUTS TO THE ARCTIC; BRACKETS INDICATE SOURCES EFFECTIVELY ISOLATED FROM THE ENVIRONMENT.

	Year	$^{239+240}$Pu Total (TBq)	$^{239+240}$Pu Arctic (TBq)	Comment
Distant Sources				
Global weapons fallout [1,3,7]	1945-1964	12 000	100 - 400	Arctic input represents direct deposition to oceans plus river run-off from land.
Sellafield [3,5,8]	1952-1995	610	2 - 20	Present sources include remobilization from contaminated Irish sea sediments.
Run-off from land-based nuclear installations [1,2,9]	1949-	2 +	?	Reported discharge from Mayak to the Techa (1949-51). Other sources include Tomsk-7 and Krasnoyarsk.
Chernobyl [1,2,10]	1986	60 - 90	< 1	More than 90 % Pu deposited with fuel particles close to the NPP
Local and Regional Sources				
Novaya Zemlya - above ground weapons tests [1,2,7]	1955-1962	2000-8500^a	5-10 "close in"	Total 87 tests, including the 58 Mt H-bomb 3rd October 1961
Underwater tests [6]	1955-1961	? - kilotonne yield		Up to 15 kBq/kg in Chernaya Bay sediments.
Underground tests [1]	1963-1989	(730^a)		Total 343 tests. Some releases.
Dumped waste and nuclear reactors [3,11]	1961-1984	(9)		Majority of actinides still isolated within spent reactor nuclear fuel and weapons (Komsomolets).
Komsomolets (Bear Isl.) [11]	1989	(20)		
Thule (Greenland) [1,12]	1968	8 - 15 TBq total ~1 TBq after clean up		US B-52 bomber carrying four Pu-nuclear weapons.

a - Calculated from estimated Cs-137 releases; assumed Pu-239+240/Cs ratio = 0.013 (global fallout at time of deposition)

3. RESULTS AND DISCUSSION

3.1. Analytical performance

Results of plutonium measurements are given in Table 2. The high sensitivity of AMS enabled determination of ^{239}Pu and ^{240}Pu in all samples. Procedural blanks gave count rates of less than 3 counts per hour for the anion exchange samples. Since a sample containing 2 mg Fe can be counted for at least one hour, this corresponds to an absolute detection limit [17] of less than 1 fg Pu. For the isotope count times of the present run (max 15 mins), the effective detection limit was 4 fg Pu, or about 10 µBq ^{239}Pu per sample. These limits compare favourably with other low-level Pu mass spectrometric methods such as high sensitivity ICP-MS [18] and thermal ionisation mass spectrometry (TIMS) [19]. $^{239+240}$Pu activities in the samples were calculated from the measured 239/242 and 240/242 atom ratios, using half-lives of 24,110 yr for ^{239}Pu; 6563 yr for ^{238}Pu, and 3.75 x 10^5 yr for ^{242}Pu [20]. For the leached planchettes, $^{239+240}$Pu activities from accelerator mass spectrometry showed excellent correlation with alpha spectrometry results (AMS = 0.9925*ALPHA; R^2 = 0.999, n=5). The 242/239 isotope ratio precision of the CRM was 0.7 % (relative standard deviation, n=5), which was in good agreement with that expected from Poisson counting statistics, 0.6 %.

3.2. Plutonium isotope ratios in Kara Sea and Novaya Zemlya samples

For Northern areas, literature data on plutonium isotope ratios in global fallout range from 0.176 to 0.190 for ^{240}Pu/^{239}Pu [21,22] and from 0.02 to 0.04 for ^{238}Pu/$^{239+240}$Pu [13,15,23]. Looking at the Kara Sea and Novaya Zemlya samples, it is clear that most samples showed similar ratios to the published global fallout levels [Table 2; Fig. 1]. However, perturbations from fallout ratios were seen at a number of sites, most notably the Abrosimov Fjord and Yenisey Estuary where ^{240}Pu/^{239}Pu atom ratios were between 0.13 and 0.14, and Stepovogo Fjord where ^{240}Pu/^{239}Pu ratios of up to 0.28 were observed. High ^{238}Pu/$^{239+240}$Pu ratios were also seen in some Stepovogo and Abrosimov sediments.

As already pointed out, source term information can be derived from data on plutonium isotope ratios; and these ratios are known to vary with factors like nuclear fuel burn-up, reactor type and operating history, neutron flux and weapon yield. In light of the number of different Pu sources to the Kara Sea [Table 2], and the variations between sources and sites, the following discussion of results has been divided into two parts. The first part covers sites and sources with low ^{240}Pu/^{239}Pu ratios (as compared to global fallout), the second part sites and sources with high ^{240}Pu/^{239}Pu ratios.

3.2.1. Low-burnup, low-yield Pu sources: Ob, Yenisey, Kara Gate and Abrosimov Fjord

Weapons-grade Pu is characterised by low ^{240}Pu/^{239}Pu ratios, usually with a ^{240}Pu content no greater than 5 % [24]. The Ob and Yenisey Rivers both have a number of weapons-grade Pu sources in their catchment areas, including the Russian plutonium production and reprocessing plants at Mayak, Tomsk-7, and Krasnoyarsk, and the Semipalantinsk nuclear weapons testing site in Kazakstan. However, most of these installations are situated more than 2000 km from the estuary. The present study indicated an influence from a low ^{240}Pu/^{239}Pu source in the Yenisey Estuary and, although representing only one sample, the observed isotope ratio showed good agreement with published data [25,26]. Measurement of Pu isotope ratios Ob surface sediments gave no evidence for significant non-global fallout sources. This is in line with other reported observations [25,26]; although, low ^{240}Pu/^{239}Pu ratios have been identified in sub-surface Ob sediment samples [27].

Joint Norwegian Russian Investigations identified enhanced Pu concentrations and high Pu/Cs ratios (relative to global fallout) in sediment samples from SW of the Kara Gate [2]. A probable source of Pu at this site is the underwater nuclear weapons tests carried out in Southern Novaya Zemlya. Sediments from the nearby Chernaya Bay are known to be highly contaminated (up to 15 kBq/kg), and a ^{240}Pu/^{239}Pu atom ratio of 0.030 has been reported, indicating low yield tests [6]. Previous analysis of the Kara Gate samples showed that ^{238}Pu/$^{239+240}$Pu ratios were similar to global fallout [2]. The present study showed a ^{240}Pu/^{239}Pu atom ratio of 0.16±0.03, from which it can be calculated that up to 40 % of the Pu could originate from a source having a ^{240}Pu/^{239}Pu ratio of 0.03. The high uncertainty reflects poor counting statistics for this particular sample; other samples from the profile are under analysis.

Plutonium sources to the Abrosimov Fjord include dumped radioactive waste containers, reactor compartments both with and without spent nuclear fuel (three submarine pressurised water reactors, PWR), and close in fallout from Novaya Zemlya tests. Of these sources, estimates of Pu-isotope ratios are available only for the reactor compartments, and these are based on computer calculations using available information on the reactor type, fuel composition and burn-up [reviewed in ref. 3]. All reactors dumped at Novaya Zemlya had suffered some form of accident, hence fuel burn-up times were relatively low [11], while the relatively high ^{235}U enrichment used in marine PWRs (7-20 %) enhances production of actinides [28]. Recent calculations put the ratios in Abrosimov reactors at 0.13 (atom ratio) for $^{240}Pu/^{239}Pu$ and 0.45 (activity ratio) for $^{238}Pu/^{239+240}Pu$ [3]. Enhanced Pu concentrations were seen at only one site in Abrosimov: close to radioactive waste containers, and the Pu-isotope ratios at this site were rather constant [Figure 2]. Subtracting global fallout gives a calculated $^{240}Pu/^{239}Pu$ ratio in the 'contaminating source' of between 0.07 and 0.12; while the corresponding $^{238}Pu/^{239+240}Pu$ ratio would be greater than 0.4. The low $^{240}Pu/^{239}Pu$ ratios suggest a non-civil source, while the high $^{238}Pu/^{239+240}Pu$ ratio should exclude waste from Pu weapons production. Analysis of sediments collected from other sites, showed no significant deviation in Pu-isotope ratios.

3.2.2. High burn up, high yield sources: Stepovogo Fjord.

Potential plutonium sources to Stepovogo are similar to those at Abrosimov, although in this case the dumped waste includes two liquid metal reactor compartments within a scuttled nuclear submarine (90 % ^{235}U enrichment and burn-up of 0.88 GW_d). The low burn-up and high ^{235}U enrichment is reflected in the calculated isotope ratios: 0.0055 for $^{240}Pu/^{239}Pu$ and 0.12 for $^{238}Pu/^{239,240}Pu$ [3,11]. The longer nuclear fuel is left in a reactor, the higher the ratios of both ^{240}Pu and ^{238}Pu relative to ^{239}Pu. Thus, $^{238}Pu/^{239,240}Pu$ activity ratios civil reactor or reprocessing sources are about an order of magnitude greater than global fallout, and have proved useful in monitoring the migration of Sellafield-derived Pu [5]. However, Pu-isotope ratios in high burn-up civil reactors can differ from those in naval reactors. This is well illustrated by the Pu-isotope ratios measured here in Cap La Hague effluent, and previously published data for the Sellafield reprocessing plant and Chernobyl reactor [Table 2].

TABLE II. AMS AND ALPHA-SPECTROMETRY MEASUREMENTS [2,9] OF PU ISOTOPE RATIOS IN KARA SEA AND NOVAYA ZEMLYA SEDIMENTS, AND COMPARISON WITH PUBLISHED VALUES FOR VARIOUS SOURCES.

Site	Site	$^{239+240}Pu$ (Bq/kg DW)	$^{240}Pu/^{239}Pu$ (atom ratio)	$^{238}Pu/^{239+249}Pu$ (activity ratio)
Sediments				
Open Kara	Surface sediment (n=3)	0.06 - 1.41	0.16 - 0.20	0.023 - 0.041[a]
Kara Gate	Surface sediment	2.2 + 0.1	0.16 ± 0.03	0.02 - 0.04[a]
Abrosimov Fjord	Close to containers (n=3)	2.3 - 4.2	0.132 ± 0.006	0.5 ± 0.1
	Inner Fjord	0.98 + 0.05	0.177 ± 0.018	0.025
	Outer Fjord	0.31 + 0.02	0.20 ± 0.02	0.030
Stepovogo Fjord	Inner Fjord (n=3)	0.62 - 9.8	0.17 - 0.28	0.045 -0.18
Ob Estuary	Surface sediment	0.72 + 0.06	0.192 ± 0.019	n.a.
Yenisey Estuary	Surface sediment	1.09 + 0.04	0.142 ± 0.018	n.a.
Sources				
Global Fallout - Northern Hemisphere [21-24]			0.175 - 0.19	0.025 - 0.04
Reprocessing Plants				
Sellafield	Surface sediment		0.22	0.19
	Sediment profile [29]		0.05 - 0.25	
Cap la Hague	Effluent - this study		0.34 ± 0.03	0.36
Chernaya Bay [6]			0.030	
Thule [13]			0.033 - 0.055	0.015 - 0.025
Mayak	Upper Techa [30]		0.013 - 0.024	0.005 - 0.018
	EURT [20, 30]		0.026 - 0.028	0.011 ± 0.02
Chernobyl - fuel particles [10,24]			0.45 - 0.52	0.48

a - Includes additional samples to those than analysed for *240/239* Pu ratios; n.a. - Not analysed

Samples from the inner part of the Stepovogo Fjord (close to dumped containers) showed high ratios for both ^{240}Pu/^{239}Pu and ^{238}Pu/^{239,240}Pu, respectively, 0.17-0.28 and 0.04-0.18. This combination indicates Pu originating from high-burn up, civil sources, however, the inhomogenity of the ratios suggest more than one source [Table II; Fig. 1].

4. CONCLUSIONS

Although based on relatively few samples, this pilot study has shown that deviations from global fallout ^{240}Pu/^{239}Pu ratios can be identified in sediments collected from dumping sites at Novaya Zemlya. It appears that an influence from low burn-up or non-civil sources is apparent in the Yenisey Estuary and Abrosimov Fjord; while the ratios seen in contaminated sediments in Stepovogo Fjord are concurrent with high burn-up, civil sources. The data support further investigation of the samples, and future AMS studies will be carried out to obtain more information on the distribution of Pu-ratios within specific sites data on other Pu isotopes and actinides.

The generally low levels of radionuclides in Arctic sediments, often combined with limited sample sizes, necessitate reliable low-level techniques for determination of Pu-isotopes. Accelerator mass spectrometry has proved to be a powerful method for measuring low-level Pu activity concentrations and Pu-isotope ratios. Absolute detection limits of a few fg Pu can compete with both TIMS, high sensitivity ICP-MS, and certainly alpha spectrometry, while showing less interference, memory and matrix effects as compared to routine ICP-MS techniques. Although the method is unable to match TIMS for precision on isotope ratio measurements, it does have the advantage of a somewhat faster sample throughput (30 - 60 per day) and significantly lower cost.

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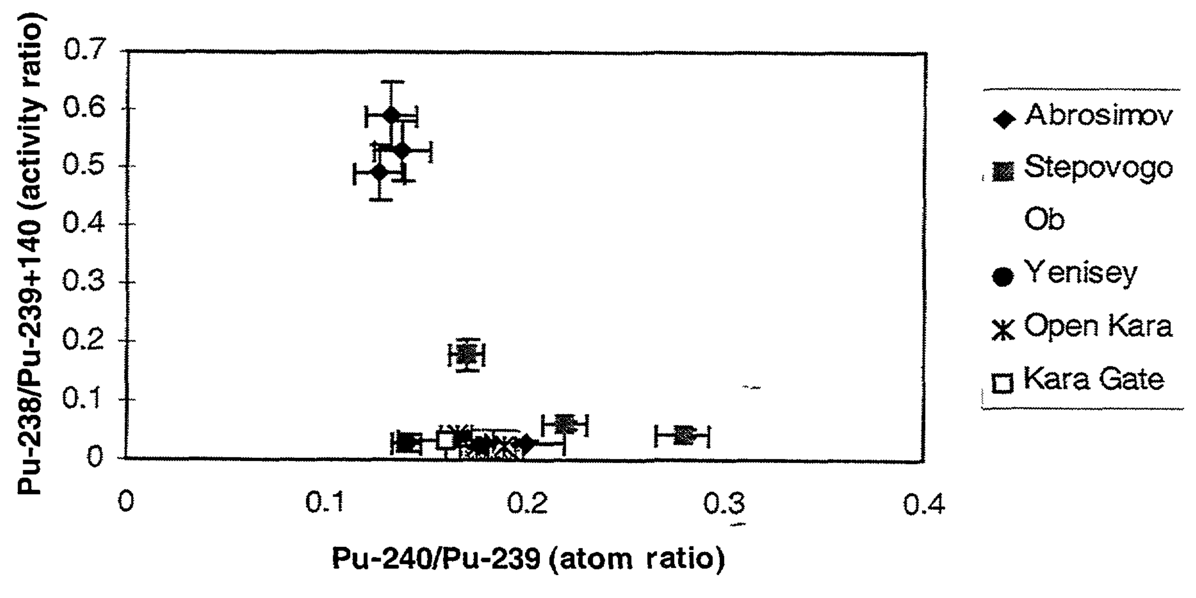

FIG. 1. Plutonium isotope ratios in sediment samples from the Kara Sea and Novaya Zemlya; --- reflects fallout ratios.

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ORGANOCHLORINE POLLUTANTS LEVEL IN TELEOST FISH AND BIVALVE FROM EGYPTIAN MEDITERRANEAN COAST AND NILE ESTUARY

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Abstract

Residue levels of 15 organochlorine pollutants and 3 aroclors were analyzed by capillary Gas Chromatography GC in fish *Mugil cephalus* and bivalve *Donax sp.*, collected from three different locations, at El-Mex bay, Balteem and Rosetta. The studied pollutants were DDT's isomers, HCHs isomers as well as cyclodiene compounds, Mirex, methoxychlor, toxaphene and hexachlorobenzene (HCB), Aroclors 1248 1254 and 1260 in addition to 10 individual PCBs congeners. Lipid content percentage ranged from 2.2 to 3.6% in fish and 1.0 to 1.5 % in bivalve, as judged by extractable Organic Matter (EOM) values. Lindane dominated the alph-isomer, with highest concentration 4.6 ng/g in fish from El-Mex. p,p'-DDE dominated other DDTs analogs with the highest concentrations in fish 15.6 ng/g) and bivalve (9.9 ng/g) from Rosetta. Toxaphene was detected in all locations with maximum levels 13.0 and 11.0 ng/g in bivalve and fish respectively, from Rosetta. Aroclor 1248 dominated other aroclors in both fish and bivalve. For individual PCBs 153 congener dominated other congeners with lower chlorinated biphenyls (mono- through penta- chloro-biphenyls) congeners occurred at lower levels except PCB 200 and PCB 206.

1. INTRODUCTION

Numerous reports are found on organochlorine residues in the Egyptian coastal marine environment, however, not for toxaphene, which was heavily used in early sixties, [1-6] reported heavy use of toxaphene (54,000metric tons), endrin (10,500 metric tons) and DDT (13,500 metric tons). Toxaphene is a complex mixture of chlorinated terpenes, probably hepta-, octa-, and nona-chlorobornanes [7], with the analog (2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,8,9,10,10-nonachlorobornane), being used as a toxaphene marker in GLC analysis.

This investigation was undertaken to determine the residues of the studied organochlorine pollutants (see Table 1) in fish *Mugil cephalus* and bivalve *Donax sp.* Collected from, El-Mex, Balteem, and Rosetta local markets.

2. MATERIALS AND METHODS

Samples extraction and clean up were describe elsewhere [8]. A tissue sample (15.0g, wet weight) was spiked with (2,4,5-trichlorobiphenyl (TBC) internal standard 1.0 ml (50.0 µg/ml), ground with anhydrous sodium sulphate (100 g) to a free flowing powder, slurry packed into a column filled with dichloromethane:n-hexane mixture (1:1), and eluted with additional solvent 300 ml (3-5 ml/min). The eluate was rotary evaporated to 10.0 ml and dried on anhydrous sodium sulphate, then Extractable Organic Matter (EOM) was determined. The extract (10.0 ml) was evaporated by a steam of nitrogen to 1.0 ml and loaded onto a gel permeation column (Biobeads SX-3 60 g) and lipids removing was performed using dichloromethane: n-hexane mixture (1:1, 150-300 ml). The collected fraction was rotary evaporated down to 10.0 ml, then nitrogen concentrated to 1.0 ml prior fractionation.

Polychlorinated biphenyls (PCBs) separation was done on a deactivated (1.5%) silica gel (Merk-Germany) column (230 mm x 7 mm i.d.), and eluted with hexane: toluene (65/35) mixture (10.0 ml), followed by toluene (10.0 ml) and then hexane (2.0 ml). The first fraction (PCB fraction) contained TCB, PCBs congeners, Aroclors, HCB, heptachlor, mirex, and most o f the p, p'-DDE, while the second (pesticide fraction) contained the remained of DDE, p,p'-DDT p,p'-DDD, DDMU, α-endosulfan, endrin, dieldrin and methoxychlor. The eluate fractions were similarly concentrated as the raw extraction to 1.0 ml, except the second fraction which was concentrated down to dryness using a gentle stream of nitrogen, and each sample was dissolved in hexane (3.0 ml) prior to gas chromatographic analysis.

Residues were analyzed, using a HP 6890 series II GLC equipped with a ^{63}Ni-electron capture detector, SE-45 capillary column (30m x 0.25mm id),with column nitrogen flow of 1.5mL/min. and detector make-up flow of 30ml/min. The injector and detector temperatures were kept at 210 and 280 ^{o}C respectively. Initial column oven temperature was 70 °C (2 min hold) raised to 260 °C final temperature (3 °C/ min and 5min hold). Quality assurance measures included analysis of reagent blank with each set of analyses and spike samples. Residues were corrected for percent recovery (80 to 88%) except toxaphene (78 %). Components identification and determination were matched against authentic standards (BDH grade). All solvent used were supplied by Merk (pesticide grade). Peak interference was identified on a Finnigan Incos 50B mass spectrometer equipped with a varian 3400 gas chromatography and a 60 m 0.25 mm i.d DB-5 column (J & W Scientific) connected directly into the ion source. The MS was operated in the negative ion mode with methane reagent gas (UHP grade) at 0.9 torr source pressure, 110 eV, maintaining the ion source at 100 °C.

3. RESULTS AND DISCUSSION

The analytical results for studied compounds in *cephalus* and *Donax* from three studied locations are represented in Table II. For proper and easy data handling a general overview of the state of pollution is presented by advancing a grand total GT value that adds all found concentrations of organochlorine pesticides and Aroclors (see Table1). General trends were indicated from TableII. The GT values were higher in *cephalus* from the different location than *Donx,* this can be due to different lipid contents (as judged by EOM values), and also, can be due to feeding habits of *Mugil cephalus* and *Donax sp.* The values of GT were followed descending order: El-Mex> Rosetta> Balteem in both studied biota, (Table II). Table II reveals specific trend between GT values, and body size or fat content (as judged by the EOM values) of the studied fish. However, such trend was reported also for other fish species [9, 10, 4, 3, 6]. Table II reveal remarkable variation between locations with respect to the GT values, with the highest GT values at El-Mex in fish (183 ng/g) and bivalve (110 ng/g). The results in Table II indicated generally that, total Aroclors represents the most abundant group of compounds in both organisms, from Balteem and El-Mex where its concentration represents about < 60% from the Grand total (GT) except *Donax* from Balteem. However, total pesticides concentration in Rosetta area is the most abundant group for both organisms, where it represents 54% and 61% from GT values for both fish and bivalve, respectively. These results can be attributed to occurrence of the national pesticides factory at Kaffer El-Ziate as well as high volumes of agricultural waste which discharge along Rosetta branch.

3.1. Organochlorine pesticide results

The prominent presence of DDT's isomers as compared to other studied pesticides grouping is evident, Table II. Total DDT isomers concentrations in fish represent from 30 to 50% from the total concentration of studied pesticides (TP), whereas this values were ranged from 34 to 53% in bivalve, (Table II). On the other hand, cyclodiene compounds (based on corresponding total pesticides values), was ranging from 18% to 30% at all analyzed samples, Whereas, percentage of 18% was noted for Rosetta for both fish and bivalve. HCH's isomers concentrations represent from 8 to 13% from TP concentrations for fish (Table II) and from 12 to 15% for bivalve (Table II).

The expressed notable presence of total DDT corresponds mostly to p,p'-isomer of DDE and DDT, while, *less frequent presence of p,p'-DDD is evident, in both studied biota at the studied locations* (Table II). In fish p,p'-DDE concentrations were ranging from 3.0 - 15.0 ng/g, while ranged from 3.0 to

TABLE I ORGANOCHLORINE HYDROCARBONS MEASURED IN FISH AND BIVALVE

Residue	Chemical name
HCB	Hexachlorobenzene
γ-HCH	γ- isomer of 1,2,3,4,5,6-hexachlorocyclohexane
α-HCH	α- isomer of 1,2,3,4,5,6-hexachlorocyclohexane
α-Endosulfan	α-isomer of 6,7,8,9,10,10-hexachloro-1,5,5a,4,6,9,9a-hexahydro- 6,9-methano-2,4,3-benzo(e)-dioxathiepin-3-oxid
Methoxychlor	2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Heptachlor epoxide	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene
Endrin,	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene
Dieldrin	1,2,3,4,10,10-hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-5,8-dimethanonaphthalene
p,p'- DDE	2,2-bis(p-chlorophenyl)-1,1-dichloroethylene
p,p'- DDD	2,2-bis(p-chlorophenyl)-1,1-dichloroethane
p,p'- DDT	2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane
Mirex	dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd)pentalene
Toxaphene,	2-exo,3-endo,5-exo,, 6-endo, 8,8,9,10, 10- nonachlorobornane
PCBS congeners	
PCB-1	2-chlorobiphenyl
PCB-8	2,4'-dichlorobiphenyl
PCB-28	2,4,4'-Trichlorobiphenyl
PCB-52	2,2',5,5' -Tetrachlorobiphenyl
PCB-101	2,2',3,4,4',5-pentachlorobiphenyl
PCB-138	2,2',3,4,4',5-Hexachlorobiphenyl
PCB-153	2,2',4,4',5,5'-Hexachlorobiphenyl
PCB-180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
PCB-200	2,2',3,3',4,5',6,6'-octachlorobiphenyl
PCB-206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

10.0 ng/g in bivalve. These result agrees well with that reported by [1, 2, 6, 4 3]. Whereas presented results disagree with Abd-Allah (1994) in Abu-Quir, and Abd-Allah and Ali, (1994) in El-Mex. They reported p,p'-DDE and p,p'-DDD to dominate other analogs, the studied fish was not included.

Aldrin and deildrin constitute most of the studied cyclodiene's concentrations found in fish from El-Mex (6.9 and 4.1 ng/g), and bivalve (3.8 and 3.1 ng/g) from Rosetta, respectively, (Table II). Presented results disagree with [4] in [3] in El-Mex in which they reported the dominance of heptachlor than aldrin but in different fish. Heptachlor epoxide occurred at high levels than heptachlor that is can be due to rapid conversion of heptachlor to more polar metabolites, The found results agrees well with what reported by [2, 6], *Mugil cephalus* was not included.

Gamma-isomer (Lindane) dominated the alpha-isomer. Hexachlorocyclohexane (HCH) (Lindane) was present in all samples with maximum levels in fish (4.6 ng/g) from El-Mex (Table II) and in bivalve (4.1 ng/g) from Rosetta, (Table II). These results agree with that results reported by [6]. Although alpha-isomer more persistent than gamma-isomer and is accumulating in fish to a greater extent than lindane, the present data indicate that the dominance of lindane in all samples, that is reflect the continuing use of this isomer in our environment for variety of applications.

TABLE II TOTAL CONCENTRATIONS OF ORGANOCHLORINE COMPOUNDS (ng/g) IN FISH

Fish	*Mugil cephalus*			*Donax sp.*		
AREA	**Balteem**	**El-Mex**	**Rosetta**	**Balteem**	**El-Mex**	**Rosetta**
Lenght	12.5 ±1.0	±1.3	±1.7	1.0	1.1	1.5
Weight	90.0±1.3	108.0 ±2.4	105.0 ±4.0			
Samples No.	16	16	16			
% HEOM^{a}	2.2	3.6	2.9			
Grand total	61.0	183.2	112.3	31.8	100.8	83.1
Total pesticides	22.8 (37%)^{b}	62.7 (34%)^{b}	60.4 (54%)^{b}	14.6 (46%)^{b}	34.5 (34%)^{b}	50.9 (61.3%)^{b}
Total Aroclors	33.2 (63%)^{b}	120.5 (66%)$_{b}$	51.9 (46%)^{b}	17.8 (56%)^{b}	66.3 (66%)^{b}	32.2 (39%)^{b}
Total DDTs	6.9 (31%)^{c}	23.6 (38%)^{c}	30.5 (50%)^{c}	7.7 (53%)^{c}	11.7 (36%)^{c}	20.6 (41%)^{c}
ΣCyclodienes	6.8 (30%)^{c}	18.5 (30%)^{c}	10.7 (18%)^{c}	3.4 (23%)^{c}	9.3 (29%)^{c}	9.4 (18%)^{c}
Total HCHs	2.9 (13 %)^{c}	7.4 (12 %)^{c}	4.8 (8 %)^{c}	2.2 (15 %)^{c}	4.8 (15 %)^{c}	6.2 (12%)^{c}
ΣPCBs congeners	12.1	87.7	30.6	7.8	34.1	21.1
HCB	0.5	4.2	1.7	N.D	1.3	0.7
γ-HCH	2.0	4.6	3.2	1.6	3.3	4.1
α-HCH	0.9	2.8	1.6	0.6	1.5	2.1
α-Endosulfan	N.D	1.8	N.D	N.D	1.1	N.D
Methoxychlor	1.1	2.3	1.2	N.D	0.7	0.9
Heptachlor	1.5	2.4	1.6	N.D	0.7	0.7
Heptachlor epoxide	2.1	3.5	3.2	0.5	2.0	1.3
Aldrin	2.4	6.9	4.3	1.5	3.1	3.8
Endrin	0.3	1.6	N.D	N.D	1.3	0.5
Deildrin	0.5	4.1	1.6	1.4	2.5	3.1
p,p'-DDE	3.3	10.9	15.6	3.6	5.8	9.9
p,p'-DDD	1.4	3.8	4.8	1.7	2.2	4.2
p,p'-DDT	2.2	8.9	10.1	2.4	3.7	6.5
Mirex	0.4	1.1	0.9	N.D	1.4	0.3
Toxaphene	4.2	3.8	10.6	1.3	3.9	12.8
Ar 1248	20.8	55.6	31.9	9.1	31.2	15.3
Ar 1254	12.4	40.2	10.4	6.4	20.7	10.2
Ar 1260	5.0	24.7	9.6	2.3	14.4	6.7
PCB Congeners						
1	N.D	0.7	0.3	N.D	1.4	0.1
8	N.D	2.1	N.D	N.D	2.6	1.6
28	1.5	4.8	2.2	1.0	3.9	2.4
52	N.D	12.9	2.6	1.3	4.6	2.4
101	3.3	14.5	6.3	1.4	3.3	1.7
138	4.1	17.8	8.4	0.9	N.D	1.8
153	1.0	19.1	6.3	2.3	14.4	6.7
180	2.2	10.3	3.0	1.5	5.4	4.9
200	N.D	5.5	1.5	N.D	1.6	1.1
206	N.D	N.D	N.D	N.D	1.3	N.D

a: extractable organic matter , based on fresh weight of the living organism.

b: based on Grand total c: based on Total of Pesticides

GT = Grand total = Total pesticides +Total Aroclors N.D = not detected

Hexachlorobenzene (HCB) occur in environment as a result of this compound's wide used as a fungicide and because it is a by-product of the production of other chlorinated hydrocarbon [11].. In some Mediterranean fish species collected in September 1983 at Port Said, Egypt, the concentration levels of HCB ranged from 0.1 to 18.4 ng/g [1]. Whereas, the present data revealed that, HCB highest level occurred in fish from El-Mex, 4.2 ng/g, and being 1.3 ng/g in bivalve, (Table II).

The relatively less significant presence of α-endosulfon is evident (Table II). It detected only in fish and bivalve from El- Mex (1.8 and 1.1 ng/g respectively), however, no peaks were observed in other biota samples. Methoxchlor, a widely used DDT analog registered for a variety of applications, occurred in all studied samples except in bivalve from Balteem, with a maximum level in *cephalus* from El-Mex 2.3 ng/g. [2] failed to detect α-endosulfon in five species from Abu-Quir, whereas methoxchlor ranging from 0.2 to 2.0 ng/g, (Table II).

Mirex is known for its insecticidal activity and more widely used as flame retardant and plastisizer [12]. Hence, its persistence in the environment and retention by fish [13], which supports its wide presence at all locations except in bivalve from Balteem, with maximum levels 1.1 ng/g in fish from El-Mex and 1.4 ng/g in bivalve(Table II).

Substantial unknown peaks interference hindered GLC-ECD identification of toxaphene constituents in fish and bivalve at all locations. One major marked peak is dominant and assigned as polychlorobornane (CHB) as being identified by GC/MS full scan electron capture negative ion mode (ECNI).

Table II illustrated that Rosetta bivalve *Donax sp.* attained a maximum toxaphene value of 12.8 ng/g, (represented 25% of TP in Rosetta) as contrasted with 10.6 ng/g for Rosetta *Mugil cephalus,* (represented 18% of TP in Rosetta). It is noteworthy that this is the first record of toxaphene residues and PCBs congeners in the studied areas. [7] reported high toxaphene concentrations in bottom feeding fish such as common carp, which he attributed to toxaphene relatively high vapour pressure and lipid solubility, which explains bivalve toxaphene high levels.

Toxaphene is still manufactured and used in some East European countries, Mexico, Latin, America, India and other developing countries. Therefore, it is suggested that the Global Environment Monitoring System (GEMS) established by UNEP, which include Canada, USA, Egypt and other 38 participating countries, should consider toxaphene residues as one of the organochlorine pollutants for mandatory monitoring in imported and exported food materials, [5].

3.2. Polychlorinated biphenyls (PCBs)

Table II illustrated that Ar1248 levels were more dominant than that of Ar1254 and Ar1260. The found data reflects to a great extent, the nature of local industry wastes. The highest levels of Ar1248 occurred at El-Mex in *Mugil cephalus* (55.0 ng/g), and in *Donax sp.* (31.0 ng/g). [14] reported that at least 57% of the PCB production is still in use and their future dispersal into the oceans can not easily be controlled.

Since all PCB components have different molecular structures, each component has its own physical and chemical properties, resulting in differences in their environmental fate and impact. The distribution of the PCB congeners in the studied locations exhibited a remarkable variation among species. Regarding to total concentrations of PCB congeners, the highest levels occurred at El-Mex in both fish *Mugil cephalus* and bivalve *Donax sp.*were 87.0 and 38.0 ng/g, respectively. As fare as the PCB's congeners are concerned, PCB 153 dominated other congeners in all analyzed samples with highest concentrations 19 and 14 ng/g in fish and bivalve respectively. Table II was illustrated that the lower chlorinated biphenyls (mono- through tetra-chloro-biphenyls) congeners occurred at lower concentrations. This is due to the equilibrium between fat content and PCBs type [15]. Inversely, PCB 206 being negligible in fish and bivalve except at El-Mex (Table II).

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PERSISTENT ORGANOCHLORINE POLLUTANTS (POP'S) IN COASTAL ENVIRONMENTS OF SOUTHEAST GULF OF MEXICO

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Abstract

Analyses to determine the presence and concentrations of persistent organochlorine pollutants (POP's) were carried out in sediments and estuarine organisms (*Crassostrea virginica*) from five coastal lagoons of the Southeast Gulf of Mexico. The results of this study show high levels of POP's in sediments with high concentration of Heptachlor, Aldrin, Dieldrin and ppDDT, either in sediments or biological tissues. According to national regulations, the use and dispersion of these chemical have been severely restricted o totally prohibited in developed countries, however their presence in coastal areas indicate an extensive use and recent application of them.

1. INTRODUCTION

In the last three decades, a large variety and quantity of chlorinated pesticides has been introduced into the developing countries coastal areas as a result of their use in agriculture, for protection and higher efficiency concerning harvest and decease vector control like malaria and paludism. While the application and production of those compounds has been restricted or totally banned in developed countries, they are commonly used in other regions like Central America, South America and Africa [1, 2].

Mexico presents an annual chlorinated pesticides production consisting of 4000 tons DDT and 1800 tons of Lindane, Toxaphene, Dieldrin, Chlordane and Heptochlor, which are widely used in the national agriculture [3] and are also exported mainly to Central America and Asia.

Recent environmental studies show high agrochemical concentrations in food, fruits, vegetables and milk products [4], maternal milk and in organisms of coastal areas.

Thus, the following study was carried out in order to obtain basic information about the concentration and distribution of selected chlorinated pesticides in coastal lagoons in the southeast of the Gulf of Mexico, because their ecological importance as producers and harvest centers for oysters, clams and shrimps.

2. MATERIALS AND METHODS

The study includes five important systems of coastal lagoons southeast of the Gulf of Mexico: the lagoon Alvarado in Veracruz (95°34'–95°58' W longitude and 18°14'-18°18'N latitude), Carmen-Machona located in the littoral fringe of the state of Tabasco (93°34' – 95°58' W longitude and 18°42' – 18°46' N latitude), and Terminos lagoon in Campeche State (91°00'-92°20' W longitude and 18°20'-19°00' N latitude) (Fig. 1).

The sediments samples were obtained from 25 locations within the lagoon areas using a Van Veen dredge with a 5 kg capacity; the bivalve mollusks (*Crassostrea virginica*) were taken out manually from 10 different banks in both lagoons obtaining an approximate number of 50 organisms from each bank. The analytical methods used for the extraction, purification and quantification of the chlorinated hydrocarbons were those recommended by the [5] for sediments and the [6] for organisms.

The sediments and organisms were extracted with 200 ml of bidistilled hexane for 8 hours in a soxhlet apparatus and the extract was reduced to 2 ml by rotoevaporation prior to fractionation using chromatographic columns (15 cm long., 3 cm ID) packed with 13 g of 1.25% deactived florisil and eluted with hexane and a mixture consisting of hexane-diethylether.

The volume was concentrated to 5 ml in order to be analyzed by gas chromatography using a Hewlett Packard chromatography model 5890, a 30 m x 0.25 mm ID x 0.25 µm bonded 5%-phenilthheysilicone, fused silica column was used. Nitrogen was the carrier gas with a flow 1 ml per minute, the oven temperature was programmed from 60°C to 300°C with an increase of 8°C per minute and the injector temperature was 260°C. A reference standard containing a mixture of 15 chlorinated pesticides was used.

3. RESULTS AND DISCUSION

In Mexico there is very little information dealing with the presence of chlorinated compounds in the tropical coastal areas inspite of their ecological importance and environmental impact.

TABLE I. TYPE OF SEDIMENTS AND PERCENTAGE OF ORGANIC CARBON IN SEDIMENTS FROM COASTAL LAGOONS.

STATIONS	TYPE OF SEDIMENTS	% TOC
CARMEN LAGOON		
1	Sand slime	1.26
2	Sand slime	1.17
3	Sand slime	1.37
4	Sand slime	1.30
5	Mud	1.29
MEAN VALUE		**1.28%**
MACHONA LAGOON		
1	Slime sand	1.43
2	Sandy mud	1.05
3	Slime sand	0.88
6	Mud	1.43
7	Slime sand	1.27
MEAN VALUE		**1.20%**
ALVARADO LAGOON		
1	Sand	1.02
2	Slime sand	0.66
3	Slime sand	0.74
4	Slime sand	2.05
5	Slime sand	0.85
MEAN VALUE		**1.06%**
MECOACAN LAGOON		
1	Sand	0.22
2	Sandy mud	0.96
3	Slime mud	1.32
4	Slime mud	3.46
5	Slime mud	2.84
MEAN VALUE		**1.76%**
TERMINOS LAGOON		
1	Sandy mud	0.62
2	Slime mud	1.34
3	Slime mud	1.68
4	Slime mud	2.64
5	Slime mud	2.70
MEAN VALUE		**1.80%**

According to the Official Catalogue of Pesticides in Mexico (1991), the use the Heptachlor, Dieldrin, Aldrin and Endrin has been totally prohibited, while DDT, Lindane and HCH are severely restricted; the results of this study, however, revealed the presence of the majority of the above mentioned chemical indicating either high persistence or recent applications.

Table 1, shows the type of sediments and percentage of total organic carbon in the sampling sites of the lagoon areas. The sediments have low percentages of organic carbon and the mean average in the five studied lagoon are in a range of 1.20% for Machona lagoon to 1.80% for Terminos lagoon. The main type of sediments were the sand slime and slime mud with low correlation with the concentration of POP's.

The Table II shows the mean values and standard deviation for the individual chlorinated hydrocarbons in sediments of the lagoons. The pesticides with highest concentrations were Heptachlor, Aldrin, Dieldrin, Endrin and ppDDT. The presence of these compounds indicates that the environmental conditions may originate their transformation and degradation, specially concerning that of Aldrin to Dieldrin and p'p'DDT to p'p'DDE.

The concentration of POP's in sediments of Alvarado Lagoon is almost two higher than in the other sites, and its worth to mention that the rivers discharging into this lagoon cross important industrial cities (Cordoba and Orizaba) and extensive coffee crops areas, and it is also related to the watershed dynamic. The variability in concentrations obtained also would be influenced by other factors as the type of sediments and the total organic carbon content, however, for this factor the correlation values were low significant.

TABLE II. THE MEAN CONCENTRATIONS OF POP'S IN SEDIMENTS FROM THE COASTAL LAGOONS (ng g^{-1}).

	LAGOON				
COMPOUNDS	CARMEN	MACHONA	ALVARADO	MECOACAN	TERMINOS
α HCH	0.12 ± 0.08	0.09 ± 0.04	0.47 ± 0.19	0.26 ± 0.08	0.32 ± 0.06
χ HCH	0.24 ± 0.11	0.28 ± 0.16	0.85 ± 0.08	0.62 ± 0.11	0.30 ± 0.10
β HCH	0.50 ± 0.25	0.62 ± 0.34	1.86 ± 0.60	0.54 ± 0.32	0.62 ± 0.12
Heptachlor	5.19 ± 2.30	2.30 ± 0.40	3.91 ± 1.21	2.36 ± 0.61	1.89 ± 0.26
Heptachlor Epox.	0.19 ± 0.10	0.27 ± 0.12	0.86 ± 0.14	0.68 ± 0.16	0.84 ± 0.18
Aldrin	0.70 ± 0.53	1.15 ± 0.29	2.11 ± 0.60	1.64 ± 0.24	2.60 ± 0.76
Dieldrin	6.84 ± 1.28	0.92 ± 0.22	2.44 ± 0.23	1.90 ± 0.16	2.80 ± 0.52
Endrin	2.73 ± 0.61	4.90 ± 1.40	7.80 ± 0.81	3.60 ± 0.63	4.20 ± 0.83
DDE	0.15 ± 0.07	0.26 ± 0.08	1.80 ± 0.18	1.40 ± 0.18	0.80 ± 0.16
DDT	1.48 ± 0.82	0.90 ± 0.12	2.30 ± 0.42	1.60 ± 0.26	2.20 ± 0.40
TOTAL	18.14	11.69	23.46	14.60	16.57

Table III shows the mean concentrations and standard deviation for individual chlorinated hydrocarbons in tissues of the american oyster *Crassostrea viriginica.* The accumulation and persistence of pesticides in biological tissues depend on environmental factors, content of lipids, age and sex of the organisms [7].

The values obtained were in most cases two times higher compared to the sediments and again Alvarado Lagoon shows the highest concentration (42.5 ng g^{-1}).

TABLE III. THE MEAN CONCENTRATIONS OF POP'S IN TISSUES OF THE AMERICAN OYSTER CRASSOSTREA VIRGINICA (ng g-1) DRY WEIGHT.

			LAGOON		
COMPOUND	CARMEN	MACHONA	ALVARADO	MECOACAN	TERMINOS
β HCH	0.62 ± 0.15	0.97 ± 0.16	2.08 ± 0.94	1.40 ± 0.22	0.80 ± 0.16
Heptachlor	2.10 ± 0.86	1.70 ± 0.50	2.90 ± 0.73	1.60 ± 0.30	1.80 ± 0.20
Heptachlor Epox	2.50 ± 0.44	3.20 ± 0.70	2.40 ± 0.60	2.00 ± 0.62	2.30 ± 0.36
Aldrin	2.50 ± 0.95	1.60 ± 0.10	6.70 ± 0.74	3.20 ± 0.44	1.80 ± 0.20
Endrin	1.50 ± 0.22	10.60 ± 1.16	8.00 ± 1.12	2.40 ± 0.26	3.20 ± 0.60
DDE	4.20 ± 0.86	BDL	BDL	1.20 ± 0.32	BDL
DDT	BDL	5.60 ± 0.86	1.60 ± 0.24	BDL	1.80 ± 0.26
Endosulphane II	0.80 ± 0.18	BDL	1.30 ± 0.18	0.80 ± 0.10	1.10 ± 0.18
Endosulphane II	14.90 ± 2.16	8.80 ± 0.44	17.60 ± 0.94	5.40 ± 0.70	2.80 ± 0.64
TOTAL	29.12	32.47	42.58	18.00	15.60

BDL = 0.010 ng g^{-1}

Published data [8] indicate that the oysters found on the american coasts concentrate pesticides up to two times more intensively compare to sediments due to their progressive concentration mechanisms for certain pesticides.

Previous studies carried out in Carmen-Machona and Alavardo lagoons showed lower concentration [9]. Thus, comparing both studies a clear increasing tendency of pesticides concentration can be observed with the passing years.

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FATE OF ^{14}C-LABELLED COMPOUNDS IN MARINE ENVIRONMENT

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Abstract

Model ecosystems have played an important role in predicting environmental behavior of agrochemicals. The microcosms used in these studies generally include soil units containing usual biotic components common for that ecosystem. In present studies, scope of two such ecosystems has been extended to study the fate of ^{14}C-labelled pesticides in marine environment. ^{14}C-labelled pesticides used in these studies were chlorpyrifos, DDT and HCH. Two systems were developed in laboratory simulating marine environment to study the fate of these pesticides. The first system was developed in an all glass aquarium tank with marine sediments, seawater, clams and algae and is referred to as marine ecosystem. The second system was developed to permit the total ^{14}C-mass balance studies. It contained marine sediments under moist (60% water holding capacity) or flooded conditions and it is referred to as continuous flow system. Fate of ^{14}C-DDT was studied in marine ecosystem while degradation of ^{14}C-chlorpyrifos and ^{14}C-HCH was studied in continuous flow system. ^{14}C-DDT did not bioaccumulate in clams while at the end of 60 days 50% of the applied ^{14}C-activity was present in sediment fraction of marine ecosystem. ^{14}C-HCH degradation showed about 22-26% mineralization while 45-55% of the applied activity was recovered as organic volatiles. No significant bound residues were formed. ^{14}C-chorpyrifos underwent considerable degradation in marine environment. TCP was the major degradation product.

1. INTRODUCTION

Since the introduction of DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane)as an insecticide in early 40s, organochlorine pesticides have played a major role in sustainable agriculture especially in the developing world. Many of these pesticides were later found to be highly persistent in the environment causing concern over their use. One of the major objections against DDT is that since it is fat soluble, it can get into food chain and bioaccumulate. Since oceans are the ultimate sinks for agricultural runoffs and other surface pollutants, marine ecosystems face a direct threat from such persistent compounds. Another organochlorine compound, which became integral part of intensive agriculture in late 60s was hexachlorocyclohexane (HCH). HCH is a group of 8 isomers of 1,2,3,4,5,6-hexacholorocyclohexane. The gamma isomer is having insecticidal properties and known popularly as lindane. It is known to metabolize rapidly in soil environment. However other isomers are not as readily degradable. Especially β-HCH is known to be very persistent in the environment. The residues of HCH isomers may accumulate in soils and sediments due to their low polarity. The relatively high volatility of HCH has led to global transport even into areas like arctic, which are away from civilization [1]. In 1990 it was estimated that 98% of the worldwide use of HCH was alone in India [2]. HCH loads in sediment have been reported along the coast of India [3].

Chlorpyrifos (O, O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate) is a member of the organophosphorous class of insecticides. This class now represents one of the most widely used groups of compounds for pest control all over the world [4]. Chlorpyrifos is a broad-spectrum pesticide, displaying insecticidal properties against a wide range of insect and arthropod pests. Because of its versatility, chlorpyrifos is used globally in a myriad of pest control situations. It is rapidly gaining importance in Indian agriculture especially in light of recent bans on organochlorine compounds.

Use of radioisotopes to trace the fate of pesticides in agricultural systems is well known. Various experimental setups simulating ecosystems have been reviewed [5]. Two of these simulated systems used in studies on pesticide degradation in soil ecosystems are extended to study fate of ^{14}C-labelled pesticides in marine environment. Results are presented here.

2 MATERIALS AND METHODS

2.1 Marine sediment and water

Marine sediment and seawater were collected from Trombay creek (Arabian Sea, West Coast of India). The sediment had 0.6-0.8% organic carbon. The pH of seawater was in the range of 7.5-7.7. Salt concentration was about 4.5-5%. In continuous flow system sediments were maintained under aerobic (60% water holding capacity) and anaerobic (seawater level of 3cm above the sediment surface) conditions.

2.2 ^{14}C-labelled pesticides

All labelled pesticides were provided by International Atomic Energy Agency (IAEA). ^{14}C-DDT (specific activity 923.15 MBq/mmol, phenyl ring ^{14}C-labelled, radiochemical purity 98% as checked by TLC) was used in marine ecosystem experiments. ^{14}C-HCH (sp. activity 60.83 MBq/mmol, uniformly labelled, radiochemical purity 75% as checked by TLC) was used in continuous flow system experiment. ^{14}C-chlorpyrifos (uniformly labelled, sp. activity 1.106 MBq/mmol, radiochemical purity 95.2% as checked by TLC) was used in continuous flow system experiment.

2.3 Marine ecosystem

A marine ecosystem was developed in an all glass aquarium tank to follow the fate of ^{14}C-labelled DDT. The tanks (45X29X30 cm) were filled with 20 L of seawater and 3 Kg of sediment (dry weight basis). Clam (*Katelysia opima*) and marine algae were other components of this ecosystem. Clams were purchased in local market. ^{14}C-labelled DDT in acetone was applied to the ecosystem at the rate of 3 μg/L (31.25 MBq) of the tank water. In each experimental tank there were 30-35 clams at start of the experiment. Two tanks received labelled DDT while one served as a control tank and received only equivalent amount of acetone. Samples of water, sediment, clams and algae were drawn at time intervals of 0, 2, 5, 24, and 72 hours and then after 7, 15, 30 and 60 days. Samples of clams and sediments were freeze dried and extracted with hexane in a Soxhlet extraction apparatus. ^{14}C-activity was estimated using a liquid scintillation counter (Packard Tricarb Model No. 3255) in dioxane based cocktail (PPO - 5g, naphthalene - 100g, 1,4-dioxane - 900 ml). Aliquots of extracts were further analyzed by thin layer chromatography-autoradiographic procedures to study the degradation of DDT. Remaining portion of clam extracts were evaporated to dryness to determine lipid contents. Extracted samples were subjected to combustion in a Biological Material Oxidizer (Harvey Instruments, USA) to determine the bound fraction. $^{14}CO_2$ liberated from oxidized samples was trapped in a special cocktail (β-phenylethylamine - 270ml, methanol - 270ml, toluene - 460ml, PPO - 5g, POPOP - 100mg) .

2.4 Continuous flow system

A continuous flow system [6] was used to study fate of ^{14}C-chlorpyrifos and ^{14}C-HCH in a marine environment. This system permits a mass balance of ^{14}C-labelled pesticide. ^{14}C-chlorpyrifos (0.21 MBq) and ^{14}C-HCH (0.33MBq) were applied at the rate of 1μg/g to 50g marine sediment maintained under moist or flooded conditions. A flow of CO_2-free and moisture-saturated air (5-8 ml/min) was maintained through the system using a fish pump. Ethoxyethanol traps were used to capture organic volatiles while 1N KOH traps were used for capturing $^{14}CO_2$. Polyurethane foam plugs were used to trap any other volatiles that may escape earlier trap [5]. The system was maintained at room temperature (28±2°C). Aliquots of KOH and ethoxyethanol were counted at frequent intervals. After a period of 40 and 85 days, experiments involving respectively chlorpyrifos and HCH were terminated. Sediment samples were freeze dried and extracted with hexane in a Soxhlet apparatus for 8 hours. Aliquots of hexane extract were counted in a liquid scintillation counter (Packard Tricarb TR-2100). Concentrated hexane extracts were subjected to TLC-autoradiographic procedures for further analysis. The extracted samples were subjected to combustion to determine the bound activity as described above.

2.5 Thin layer chromatography

Hexane extracts were concentrated and analyzed by thin layer chromatography. Silica gel (G) plates containing a fluorochrome indicator were used for TLC.

2.5.1 ^{14}C-DDT and ^{14}C-HCH

The solvent system was hexane: acetone: methanol: diethylamine (100:1:1:1 V/V/V/V). The Rf values for DDD, DDT and DDE were 0.37, 0.53 and 0.66 respectively. Analytical grade compounds DDT, DDE and DDD (Sigma Chemicals) were used in cochromatographic procedure. The Rf value for HCH was 0.56. Analytical grade HCH (Sigma Chemicals) was used in cochromatographic procedure. For DDT and its metabolites identification, plates were viewed under UV (190 nm) and spots were marked by comparing with standards. For HCH, plates were sprayed with Kovac's reagent and then exposed to UV (190 nm). Spot areas were marked and scraped. The scraped matter was suspended in liquid scintillation cocktail and counted to estimate ^{14}C-residues therein.

2.5.2 ^{14}C-chlorpyrifos

The solvent system was toluene: methanol: hexane (18:1:1 V/V/V) [7]. The Rf value for chlorpyrifos and TCP (3,5,6-trichloro-2-pyridinol) were 0.73 and 0.24-0.30 respectively. Analytical grade chlorpyrifos provided by IAEA was used in cochromatographic procedure. Chlorpyrifos and TCP spots were marked by comparing against standards under UV (190 nm). ^{14}C-residues in each spot were estimated as above.

2.6 Statistical analysis

Standard errors were estimated using standard statistical methods wherever necessary.

3 RESULTS AND DISCUSSION

3.1 Fate of ^{14}C-DDT in marine ecosystem

Distribution of DDT residues in various components of ecosystem is presented in Figure 1. Clams recorded maximum residues after 3 days. Sediment analysis showed that 60-65% of the applied radiolabelled residues were present throughout the period of experimentation. Product analysis revealed that DDE was a major degradation product in clams, while in sediments DDD was found to be a significant metabolite. The latter observation is consistent with the anaerobic conditions in sediment. Algae showed maximum residues of ^{14}C-DDT residues at 3 days, subsequently these residues decreased. Recently there are reports of DDT residues in sediments and formation of DDMU which is an important step in degradation of DDT [8, 9]. It is known that DDT degradation leads to formation of toxic chemicals such as DDE and DDD which are broken down by subsequent processes to DDMU and other compounds. It was difficult in our studies to separate DDMU and DDE on TLC plate as Rf values for these two compounds are very close. The degradation of about 50% of applied DDT in two months in marine ecosystem is indicative of the fact that the degradation is faster under these environmental conditions. Even faster degradation of DDT has been observed in soil system under tropical regions [10, 11]

3.2 Fate of ^{14}C-HCH in a marine environment using continuous flow system

Fate of ^{14}C-HCH was studied in marine environment using a continuous flow system. Results are presented in Table I. Extractable residues accounted for about 7 and 12% of the applied ^{14}C-activity after a period of 3 months. There was substantial mineralization under both moisture conditions. Under moist conditions 25-26% of the applied ^{14}C-activity was accounted as $^{14}CO_2$ while under flooded conditions the extent of $^{14}CO_2$ liberated was about 20-22%. The most significant part is the organic volatiles liberated during incubation. Under flooded conditions, about 55% of the applied activity was trapped in ethoxyethanol while under moist conditions about 49% of it was trapped in these traps. The attempts to identify these products on TLC plates failed indicating the possibility that these volatiles may be in gaseous form like benzene. A similar or higher rate of mineralization of ^{14}C-lindane has been reported [12] under aerobic conditions in sediments. It is evident that lindane is undergoing faster degradation in sediment hence possibility of its bioaccumulation is less. In present studies bound residues are formed only to the tune of 2 to 5% of the applied ^{14}C-activity, though earlier reports predicted that binding of lindane may play a significant role in the fate process [13, 14].

3.3 Fate of ^{14}C-chlorpyrifos in a marine environment using continuous flow system

^{14}C-mass balance of ^{14}C-chlorpyrifos in a continuous flow system is shown in Table II. It is evident from the table that this insecticide did not undergo mineralization under either moist or flooded conditions. However there was extensive degradation under both the moisture conditions. TCP (3,5,6-trichloro-2-pyridinol) was a major degradation product especially under moist conditions. Chlorpyrifos is known to undergo abiotic as well as biotic transformations in a variety of matrices [4]. The primarily important abiotic factor is hydrolytic degradation. It has been observed that the hydrolysis rate of chlorpyrifos is pH dependent. Under alkaline conditions more rapid hydrolysis has been reported. The hydrolysis product is TCP. In present studies the pH of seawater was between 7.5-7.7 and hence may cause enhanced hydrolysis. Results obtained by TLC-autoradiographic procedures revealed that under moist conditions 16% of the applied activity could be recovered as TCP while under flooded conditions this was about 32% of the applied activity. The recovery of chlorpyrifos was a mere 3% and 0.5% of the applied activity under moist and flooded conditions respectively. More bound residues were formed under moist than flooded conditions. That chlorpyrifos forms bound residues in soils is well documented [4]. The major significance of the high affinity for sorption of chlorpyrifos by soils and sediments lies in the implication it presents for the availability of chlorpyrifos for environmental transport processes. It is interesting to note here that in our earlier experiments to trace the fate of chlorpyrifos in a marine ecosystem containing clams, seawater, sediments and marine algae, no residues were observed in

TABLE I: ^{14}C-MASS BALANCE OF ^{14}C-HCH IN A CONTINUOUS FLOW SYSTEM (EXPRESSED AS % OF APPLIED ^{14}C-ACTIVITY)

Sediment	$^{14}CO_2$	Organic volatiles	PUF extracts	Extractable activity	Bound activity	Total activity
Moist	25.59±1.52	48.66±1.47	-----	7.27±0.38	4.76±0.21	86.28
Flooded	22.16±1.41	54.85±3.18	-----	12.17±0.81	2.43±0.36	91.61

TABLE II: ^{14}C-MASS BALANCE OF ^{14}C-CHLORPYRIFOS IN A CONTINUOUS FLOW SYSTEM (EXPRESSED AS % OF APPLIED ^{14}C-ACTIVITY)

Sediment	Organic volatiles	PUF extracts	$^{14}CO_2$	Extractable	Bound	Total
Moist	------	1.04±0.30	0.48±0.08	30.85±2.02	58.76±2.81	91.13
Flooded	------	0.67±0.12	0.42±0.06	42.53±0.82	49.15±1.30	92.77

sediments after 60 days [15]. Clams could have played major role in degradation of chlorpyrifos although there was no evidence of its bioaccumulation in clams. In present studies it may be said that marine microorganisms are not degrading the insecticide and hence more bound residues are formed. The sorption also depends on pH of the matrix and organic carbon fraction therein. Though the organic carbon fraction in sediments in present studies was 0.6-0.8%, the alkaline conditions with low amounts of organic carbon together might have led to formation of higher amounts of bound residues.

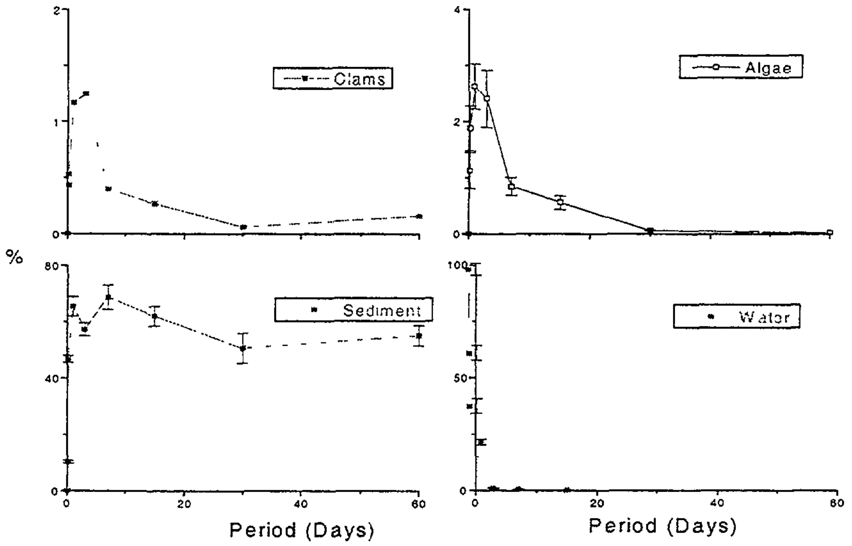

FIG 1. Distribution of ^{14}C-DDT residues in a marine ecosystem

Acknoweldgements

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AN INTERGRATED STRATEGY FOR BIOLOGICAL EFFECTS MONITORING IN SCOTTISH COASTAL WATERS

XA9951911

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Abstract

The paper summarises SEPA's current programme of water quality and biological effects monitoring and, using recent examples, discusses the current environmental issues affecting the condition of our coastal waters.

1. INTRODUCTION

The Scottish Environment Protection Agency (SEPA) is one of the main administrative bodies charged with statutory responsibility for protecting Scotland's natural environment. SEPA's principal aim is an efficient and integrated environmental protection system for Scotland which will both improve the environment and contribute to the British Government's aim of sustainable development. This is provided mainly by careful regulation of emissions to the atmosphere and aquatic environment, the management and disposal of wastes and the control of radioactive substances. Our statutory powers stem from the Environment Act 1995, a range of EC Directives and other internationally agreed obligations.

An example of SEPA's integrated approach to environmental protection is seen in the monitoring and research carried out in the tidal waters of south eastern Scotland (Fig. 1). Tidal Waters Section is a team of scientists with expertise in marine chemistry, oceanography, modelling and marine biology. The monitoring programme is achieved using a vessel " Forth Ranger", surveying most of the controlled waters of south eastern Scotland. This comprises a 600km length of coastline to a three mile limit which represents 4.5% of the total coastline of Scotland and 2.8% of that of Great Britain.

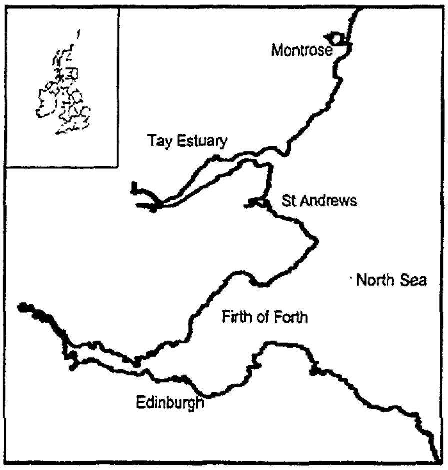

Figure 1. Map of south eastern Scotland in relation to the UK

2. BIO-DIVERSITY AND BIOLOGICAL EFFECTS

The measurement of biodiversity and habitat diversity play a central role in SEPA's assessment of environmental quality, evaluating the quality of the environment. An integrated approach to biological monitoring studies most of the key habitats and biological communities, including pelagic and demersal fish, plankton, benthic micro- and macro-algae, subtidal and intertidal macro- and meio-fauna.

2.1 Fish Communities

The fish community studies of the Forth estuary have produced one of the best and most valuable datasets for any European estuary. Since 1979 the pelagic and demersal fish populations have been monitored in detail in relation to feeding relationships [1] effects of habitat loss [2] changes in relation to water quality [3] and the importance of the estuary as an overwintering and nursery area [4]. Fish monitoring is designed to determine the effects of general water quality, persistent pollutants and the degree of food-web and habitat perturbation. SEPA currently uses a variety of trawling (benthic and pelagic) methods alongside routine examination of fish captured on the intake screens of a power station to estimate fish abundance and community structure in the Forth.

SEPA's monitoring of both fish and water chemistry in the upper Forth estuary exemplifies our integrated approach to environmental studies. In the upper Forth estuary (Fig. 7) a well documented [5] dissolved oxygen minimum develops during the summer (June-September) months when water temperatures are relatively high and river flows are generally at a minimum. The depletion of dissolved oxygen (DO) in the water column results from the degradation of organic matter, derived from both natural and anthropogenic inputs (e.g. sewage effluent) resulting in a high biochemical oxygen demand (BOD). Fig. 2 shows how an area of high suspended solids concentration develops in the upper reaches of the estuary (upstream of the freshwater/saltwater interface). Organic degradation is enhanced in this turbidity maximum leading to a sag in dissolved oxygen levels within a defined area of the estuary (Fig. 3). When concentration falls to less than 5.5 mg/l DO, the resident and migratory estuarine fish can be affected. The fish are therefore monitored throughout the summer months to estimate diversity and abundance and determine their distribution is compared with observations in previous years.

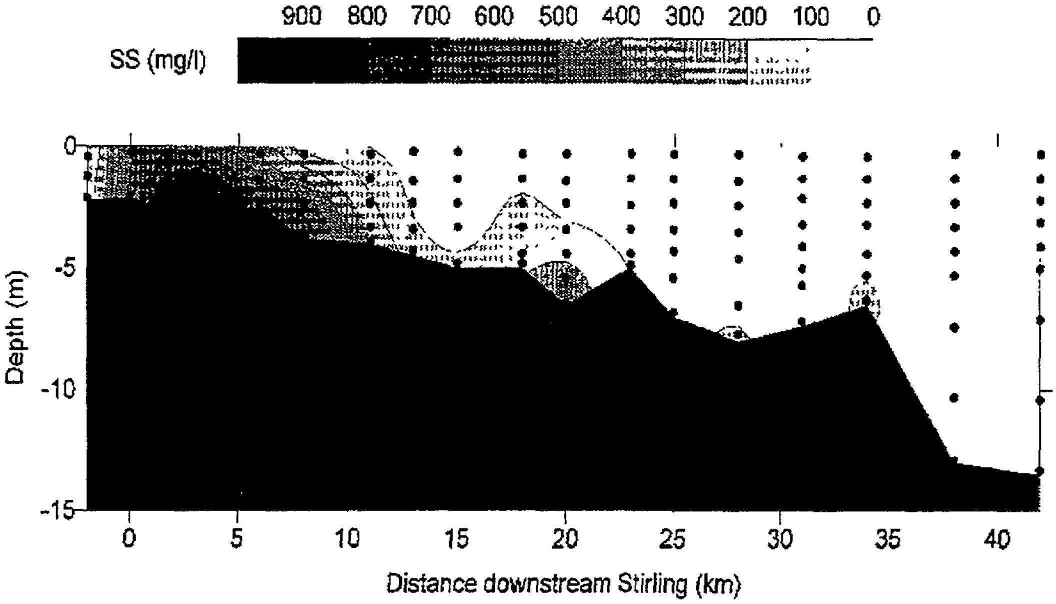

Figure 2. Distribution of suspended solids (mg/l) in the Forth Estuary on 22 July 1998 (dots represent sampling sites and depths).

Fig. 4 shows an example of these data summarised for Alloa (approximately 20 km downstream from Stirling) over the period 1996-98 (Fig.s 3 & 7). Reductions in organic inputs to the upper Forth estuary over the past decade have resulted in a general improvement in BOD and DO [6]. This improvement in water quality has been seen as the primary reason for the return of the cucumber smelt (*Osmerus eperlanus*) to the estuary following a period absence from the whole catchment.

2.2 Phytoplankton and eutrophication

Phytoplankton growth is monitored using a combination of automatic sensors (moored sub-surface and towed) and ship-based sampling. This provides detailed information on the spatial and temporal distributions of phytoplankton species and blooms in relation to major point and diffuse sources of inorganic nitrogen. This approach ensures an effective base-line of information on the dynamics of phytoplankton and nutrients, against which current and future eutrophication effects may be seen [7]. Other potential effects of nutrient enrichment are monitored, including the occurrence of abnormal toxic phytoplankton blooms and excessive growth of opportunistic macroalgae on beaches and intertidal mudflats.

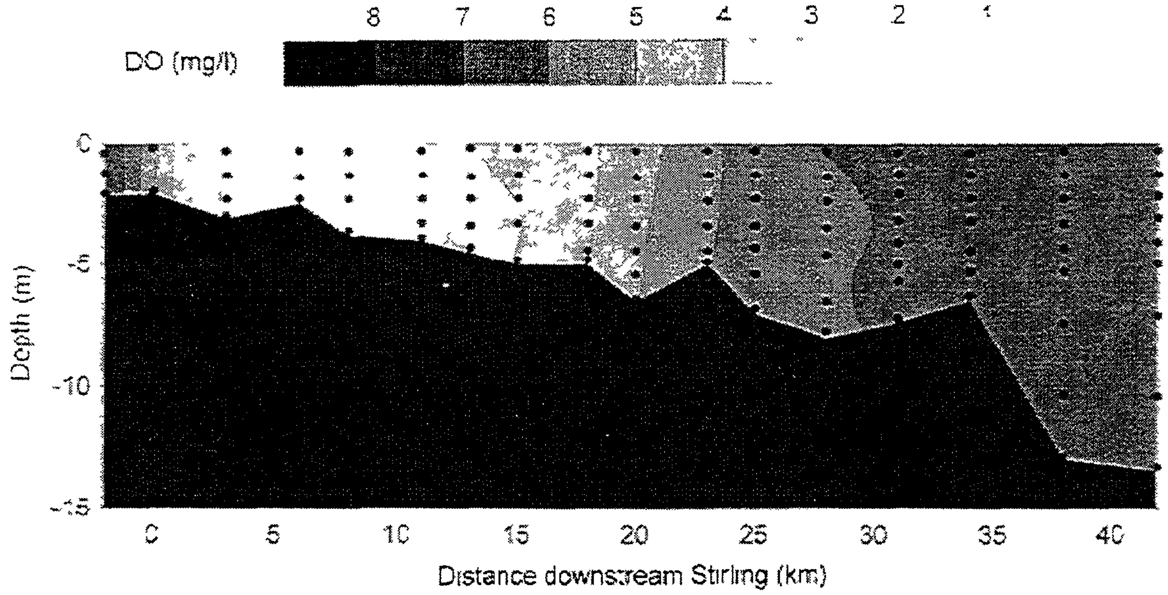

Figure 3 Dissolved Oxygen Distribution (mg/l) in the Forth Estuary
22 July 1997 (dots represent sampling sites and depths)

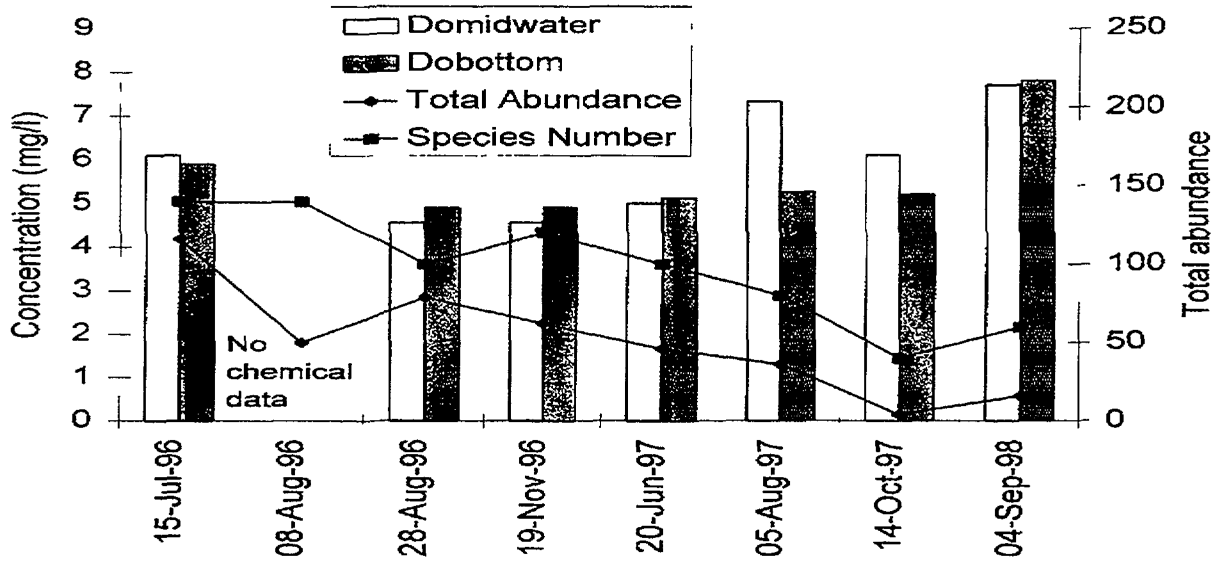

Figure 4 Fish abundance and species number with midwater and bottom water dissolved oxygen concentrations Alloa in the upper Forth estuary, 1996-98.

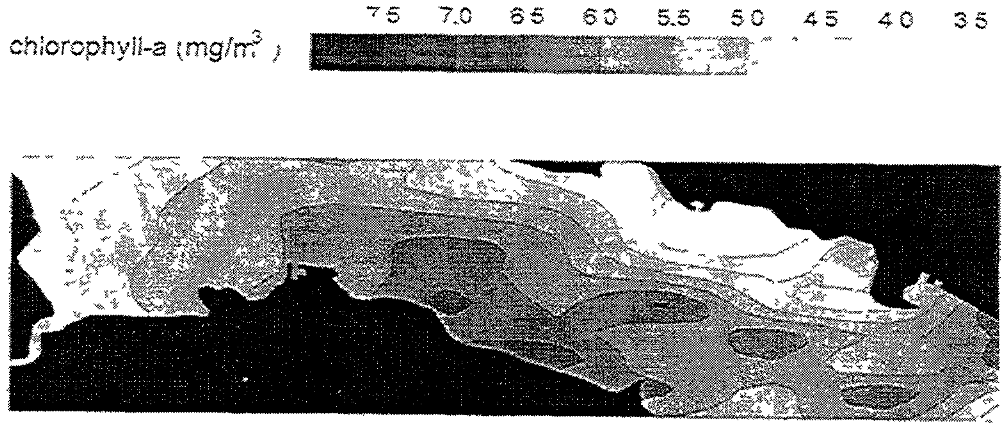

Figure 5 The spatial distribution of phytoplankton chlorophyll-a (1m depth) in the lower Forth Estuary 12th May 1997 For location see figure7

Fig. 5 shows the results of an investigation of the trophic status of the lower Forth estuary in the spring of 1997. The spatial distribution of phytoplankton chlorophyll-a was determined using a towed fluorometer, with additional sensors measuring salinity, temperature, turbidity as well as a continuous plankton recorder. This rapid mapping technique is always verified through the collection of spot samples (for salinity, temperature, suspended solids and chlorophyll-a) which also provide samples for micronutrient analysis. The distribution of phytoplankton chlorophyll-a, seen in Fig. 5, reflects the riverine input of fresh turbid water to the West (inhibiting phytoplankton production) and the tidal intrusion of phytoplankton-rich (approximately 22 mg m^{-3} chl.-a) and relatively saline water from the Firth of Forth.

Although the estuaries and coastal waters of south eastern Scotland are generally free from serious eutrophication, SEPA is tackling the underlying causes of hypernutrification. SEPA's powers of regulation allow control of the nutrient content of discharges to controlled coastal waters. Nitrogenous emissions from diffuse sources are also limited at their source by promoting Best Management Practices to the agricultural community. This initiative includes the promotion of multi-purpose buffer zones to reduce the run-off of pesticides as well as fertilisers into streams and groundwater [8]

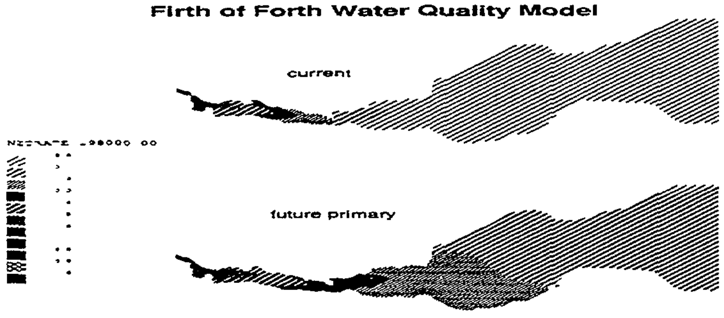

Figure 6.
Predicted nitrate levels for 50%ile current and future loads at Edinburgh and Levenmouth

SEPA also utilises a two- dimensional hydrodynamic and water quality model (TELEMAC) to investigate and predict the impact of treated effluent on the tidal waters of the Forth estuary. This model is based on both fine and coarse triangular grids enabling fine and coarse resolution to tackle both small-scale and large scale (or far-field) effects. The model is capable of simulating tidal flows and water quality processes over its domain using finite element techniques. Fig. 6 illustrates the use of TELEMAC in predicting the effect of improved sewage treatment at Edinburgh and Levenmouth Sewage Treatment Works (serving the equivalent of 1.6 million people) on the loading of nitrate within the Firth of Forth in the year 2006. These and other model runs are used as sound management tools for recommending sewage treatment levels and predicting possible biological impacts.

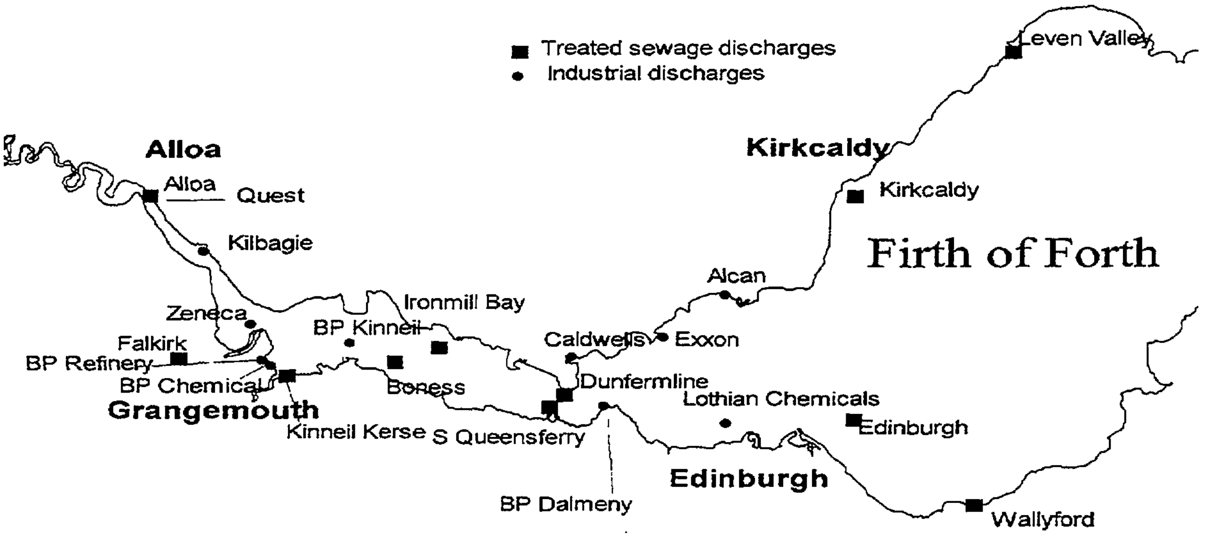

Figure 7. Major discharges in the Forth estuary and the Firth of Forth.

2.3. Benthic faunal communities

The intertidal and subtidal soft-sediment fauna are routinely examined in relation to sediment chemistry and particle size. Large spatial and temporal variations in macrofaunal abundance and species composition occur in response to natural gradients in salinity, suspended solids and sediment stability [9]. Subtle community changes are used particularly to evaluate the impact of organic waste from both sewage and industrial discharges. Fig. 7 summarises the major treated sewage and industrial discharges in the Forth estuary. The biological impact of some of these major discharges is assessed directly whereas large sampling grids are used to examine the combined impact of discharges on the health of the whole catchment. A numerical model of the settling of organic material througha moving and turbulent sea has been developed [10] to predict the effect of orgainc detritus on benthic faunal communities.

3. CONCLUSION

A long-term programme of biological and water quality monitoring has centred effort on the Forth and Tay estuaries and the coastal embayment of the Firth of Forth. The monitoring aims to assess the quality of tidal waters against quality standards set both by SEPA and EC Directives.

Sea water quality is generally defined in terms of bacterial, persistent and dangerous substances (organochlorine pesticides and heavy metals), DO, nutrient status, organic load (BOD) and suspended solids. The last three are considered the most important ecological factors, related to sewage pollution, affecting our coastal waters [11].

The measurement of contamination of sea water, sediments and marine organisms is integrated with a programme of biological effects monitoring of invertebrates, fish, macroalgae and plankton. This approach enables detailed environmental impact assessments to be made relating to both point and diffuse sources of pollution.

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METALLOTHIONEIN AS BIOMARKER OF MUSSEL EXPOSURE TO HEAVY METALS

XA9951912

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Abstract

The biological effect of marine pollution with heavy metals is followed in bivalves by means of the induced amount of metallothioneins (MTs), determined in different tissue types. The biological effect of the available toxic metals, cadmium and mercury, are related to the amount of MTs in the whole edible part, gills and the digestive gland *of Mytilus galloprovincialis*. For that purpose highly sensitive chemical and biochemical methods for metal and metallothionein content determination were developed and applied. The study was conducted in the Kaštela Bay, which is the urban and industrial center of Dalmatia, Croatia, with two groups of mussels, indigenous and the transplanted. In accordance with the objective of the Symposium the results on monitoring the marine pollution by means of MTs as a biomarker, isolated from the edible, sessile and filter-feeding bivalves are discussed.

1. INTRODUCTION

In the last two decades the study of the effects of pollutants on marine organisms has allowed the identification of a certain number of biological parameters, usually referred to as "stress indices" or "biomarkers", suitable to evaluate the physiological status of the aquatic organisms. Biomarkers have been defined as biological parameters whose variations may be utilized to point out and quantify the stress syndrome. The use of biomarkers will therefore allow the evaluation of a stress syndrome induced in the organisms by pollutants accumulated in their tissues. The use of biomarkers can therefore represent a suitable way to correlate data relevant to the concentration of chemical pollutants in marine organisms with the alteration of their physiology. Due to the rapid action of toxic chemicals at the molecular and cellular levels, biomarkers also provide an early warning for long-term pollutant effects. Finally, biomarkers are a complement to ecological surveys correlating environmental alterations to a direct effect of contaminants [1].

In this study presented are the results on the application of the inducible metal binding protein i.e. metallothionein (MT) as a biomarker for the assessment of metal exposure of mussels *Mytilus galloprovincialis* Lmk. The presented results are a novel approach, the first of this kind applied in the monitoring of the selected Croatian Adriatic seawater areas. The approach is intended as the amendment to the long-term monitoring programme of heavy metals in the coastal seawater areas, during which the metal body-burden in edible bivalves is usually followed [2]. The attempt is made to get the additional and relevant information on the biological response of the widespread, edible, sessile and filter-feeding marine organisms (*Mytilus galloprovincialis*), which are often used as the indicator organisms to monitor metal pollution of the marine and the estuarine areas.

2. MATERIALS AND METHODS

2.1. Sampling of *Mytilus galloprovincialis*

The study was conducted in the Kaštela Bay with two groups of mussels, indigenous and the transplanted ones. Sampling of indigenous *M. galloprovincialis* took place in January 1995 [3]. The stocks of transplanted mussels of defined age and origin were positioned at four stations along the Bay and were sampled from October 1997 to September 1998. For monitoring purposes the locations were selected in the coastal area of the Kaštela Bay. For mercury a defined source of pollution exists, i.e. the waste water outlet of the ex-chlor-alkali plant (station 1). At several distances from the outlet additional sampling sites were selected (stations 2A, 3A and 5A), covering the area of the Kaštela Bay. The chlor-alkali plant has terminated the production in 1990, but certain amount of mercury is still present in the sediments and is regarded as the point source. For cadmium the sources of pollution are diverse and diffuse, such as the industrial and urban waste waters and the dry/wet deposition. The physiological status of each stock of mussels has been followed by means of the basic biometric characteristics and the condition index.

2.2. Metal analysis

The study has been focused on the isolation of metallothioneins from three different tissue types and the determination of cadmium, mercury and MTs content in metallothioneins fraction. The composite samples of mussel tissue were wet digested and subsequently analyzed on cadmium and mercury content, using the appropriate methods. Mass fractions of cadmium and mercury are expressed on wet tissue basis (w_{fw}Cd and w_{fw}Hg). After digestion, cadmium content in different mussel tissue was analyzed by atomic absorption spectroscopy with the Perkin Elmer instrument model 1100B equipped with a graphite atomizer HGA 700 (GFAAS) and the automatic sample changer. The total mercury content in the digested samples of mussel tissues was determined with the cold vapor atomic absorption spectrometry (CVAAS), using a Perkin Elmer instrument model 410.

2.3. Metallothionein isolation and the analysis

The supernatant containing the heat stable MTs was isolated from the cytosolic fraction after tissue homogenization in three volumes of 0.02 mol/L TRIS HCl buffer (pH=8.6) by subsequent centrifugation at 30000xg for 40 minutes at 4°C. In order to remove the interfering high molar mass proteins, the supernatant was thermally treated for 10 minutes at 70°C, and in addition centrifuged at 30000xg for 20 minutes at 4°C. The MT content was analyzed by an electrochemical method in a differential pulse polarographic mode (DPP) on a hanging mercury drop electrode (HMDE) [4]. Presented mass fractions of MTs are expressed on wet tissue basis (w_{fw}MT).

3. RESULTS AND DISCUSSION

The uptake of metals by the filter-feeding organisms occurs via two major routes, which involve the gills (in the case of dissolved metal forms) and the digestive gland (in the case of metals associated with the ingested material such as food or sediments) [5]. In invertebrate species dissolved metals are most likely to be taken up by the gills, while the particulate metals, ingested with the food would be expected to bind first in the digestive gland cells. The gills and the digestive gland are mussel tissues involved in the process of metal uptake and detoxification. The uptake routes of these two toxic metals will be discussed.

3.1. Cadmium distribution and its biological effect

The results obtained indicate that in different **mussel tissues** the mass fraction of cadmium (w_{fw}Cd) decreases in the order:

DIGESTIVE GLAND > EDIBLE PART OF MUSSEL > GILLS

The ranges of $w_{fw}\mathrm{Cd}\times10^6$ at different sampling sites amount to:

digestive gland	0.26-0.43
edible part	0.11-0.18
gills	0.05-0.10

In the whole edible part of mussels originating from different areas of the Adriatic Sea [6] the w_{fw}Cd ranges from (0.12 to 0.19) $\times10^{-6}$. Our results reported for cadmium content in the mussel tissue from the Kaštela Bay are of the same order which indicates that the biological effect cannot be assessed by measuring the cadmium content only. The approach which gives the measure of the biological effect is explained as follows.

In the **supernatant**, which contains the heat stable MTs, the mass fraction of cadmium (w_{fw}Cd) inherent to MTs decreases in the same order as in the mussel tissue:

DIGESTIVE GLAND > EDIBLE PART OF MUSSEL > GILLS

The ranges of $w_{fw}\mathrm{Cd}\times10^6$ at different sampling sites amount to:

digestive gland	0.083-0.132
edible part	0.034-0.067
gills	0.016-0.020

The average ratio of cadmium content in the mussel tissue versus its content in the supernatant inherent to MTs amounts to 3, which means that the content of cadmium inherent to MTs amounts roughly one third of the overall cadmium content accumulated in the respective tissue. Due to the fact that cadmium inherent to MTs reflects the cytosolic level of this toxic metal, at the same time it is related to the stress effect produced by this toxic metal.

The content of MTs decreases in the same order as the cadmium content in the tissue and the supernatant, i.e.:

DIGESTIVE GLAND > EDIBLE PART OF MUSSEL > GILLS

The ranges of $w_{fw}\mathrm{MT}\times10^3$ at different sampling sites are:

digestive gland	2.84-4.23
edible part	0.85-1.25
gills	0.45-0.64.

The digestive gland of mussel *M. galloprovincialis* has both the highest inducibility and the highest extraction efficiency for MTs and is regarded as a major site for MTs synthesis. Therefore, the recommendation is to assess the cadmium effect on mussels, which are selected as indicator organisms, by measuring the MTs and toxic metal content in the digestive gland of *M. galloprovincialis*. The appropriate analysis of the field data supports the fact that in *M. galloprovincialis* a clear correlation exists between the MT and cadmium concentration [7]. Recent publication [8] indicates that the digestive gland is the preferential organ for accumulation of metals. According to [8], gills have usually the highest water content, while the digestive gland has the highest percentage of organic substance. Thus, fluctuations of metal content and consequently the MT content in the respective mussel tissue depend on the physiological and metabolic factors. Seasonal variation of trace metal content was observed in the digestive gland of *M galloprovincialis*. Highest values were recorded in the late winter-early spring time, followed by a progressive decrease during the summer. Regoli [9] explained this effect with the penetration of the gonadic tissue into the digestive gland during the gametogenesis, which actually "dilutes" metal concentration in that tissue. Bordin et al. [10] report seasonal variation of MTs content in Baltic clams and ascribe it mainly to the body weight fluctuations. The authors report the uptake of cadmium and the increase of MTs induction in winter, opposite to warmer seasons.

In Fig. 1. our selected results recorded at station 1 in the Kaštela Bay are presented, on seasonal variation of the condition index of the transplanted mussels and the MTs content in the digestive gland. The results indicate that the MTs and the metal content depend on the physiological state of the indicator organism. Therefore, the proper selection of the period for monitoring the trend of biological effect of cadmium at the cellular level of mussel tissue is important. Studying the trend of the mussel condition index, it is possible to define the reproduction period at which the emission of gametes occurs [8]. Usually, it is related to the lowest condition index. Based on our results with the transplanted mussels, *M. galloprovincialis*, it might be observed that the MTs and cadmium content in the digestive gland are 5 to 10 times higher than in the gills, which would indicate that the uptake of the particulate forms of cadmium (via ingested food, particles) is more pronounced than the dissolved cadmium forms. This conclusion needs further investigation, but the fact that the concentrations of the dissolved cadmium (10^{-10} mol/L) in the water phase do not reflect the burden of the site with cadmium might support this statement [3].

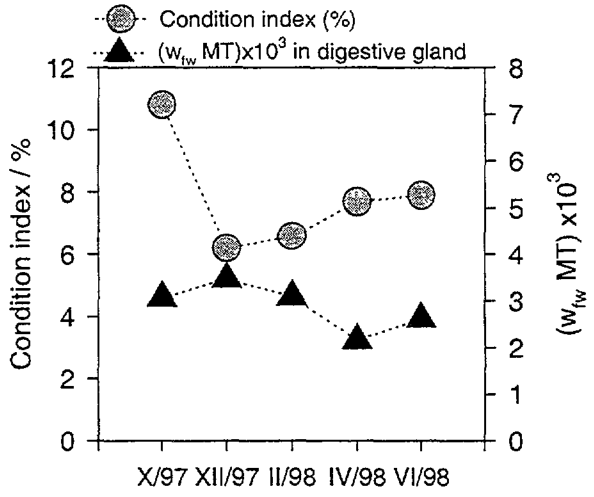

FIG. 1. Seasonal variation of the condition index (%) of transplanted mussels and the MTs mass fraction ($w_{fw}MT\times10^3$) isolated from the digestive gland. Sampling close to the outlet of the ex-chlor-alkali plant, station 1, Kaštela Bay, Dalmatia, Croatia.

3.2. Mercury distribution and its biological effect

The mass fractions of mercury ($w_{fw}Hg\times10^6$) in the composite sample of mussel tissue are strongly dependent how close is the sampling site to the source of mercury pollution, which is in this case the waste water outlet of the ex-chlor-alkali plant. Close to station 1, $w_{fw}Hg\times10^6$ is the following:

GILLS >	DIGESTIVE GLAND	> EDIBLE PART OF MUSSEL
2.69-3.00	1.77-2.80	1.50-2.35

The results indicate that close to the source of mercury pollution, the distribution of mercury within different mussel tissues is not as different as it is in the case of cadmium. Therefore, it does not seem necessary to dissect the mussels to various tissue types. Instead, the analysis of the whole edible part of mussels for mercury content seems to be appropriate. The use of mercury in the production process has terminated since 1990, but the area around the outlet of ex-chlor-alkali plant still represents a point source of mercury. This statement is supported with the obvious gradient of mercury content in seawater (450 to 14 ng/L) as the distance from the pollution source increases. Considering the mass fractions of mercury in the mussels from the Kaštela Bay, the gradient (2.35, 1.50 to 0.074) $\times 10^{-6}$ was recorded, as the distance from the point source increases [3]. In the whole edible part of mussels, originating from the unpolluted areas of the Adriatic sea the mass fractions of mercury are in the range (0.020 to 0.030)$\times 10^{-6}$ [6].

According to our preliminary results the mercury content in the **supernatant** which contains heat stable MTs follows the usual trend as for cadmium content, and that is:

DIGESTIVE GLAND > EDIBLE PART OF MUSSEL > GILLS

The ranges of $w_{fw}Hg \times 10^6$ at different sampling sites amount to:

digestive gland	0.011-0.020
edible part	0.004-0.007
gills	0.002-0.006

Further on, as could be concluded from the presented results, the partition of mercury in cytosolic fraction inherent to MTs is several times lower than for cadmium. Therefore, for monitoring the trend of mercury pollution in mussels, the suitable approach would be to analyze the mercury content in the whole edible part of mussels.

4. CONCLUSIONS

Different partitions of cadmium and mercury within the tissue of *Mytilus galloprovincialis* and the supernatant which contains MTs indicate that the sources of pollution, physico-chemical forms and the fate of these two toxic metals are different. For monitoring purposes in which mussels are used as indicator organisms, the following conditions are recommended in order to get the data from various geographical areas, which might be compared [8]:

- mussels should be collected in the same period at the end of the reproductive cycle, when the condition index is the lowest.

- preferably, the transplanted mussels of similar size, placed at the same depth, should be collected and analyzed.

In our paper presented are some results as part of the continuous study which aim is to define the levels of MTs in target tissues of *M. galloprovincialis* as biomarker of the biological effect of toxic metals on that widespread, edible, sessile and filter-feeding indicator organism.

Acknowledgement

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ECOTOXICITY STUDIES IN JAMAICAN ENVIRONMENT I. TOXICITY, BIOACCUMULATION, ELIMINATION AND TISSUE PARTITIONING OF ETHOPROPHOS BY THE FISH *TILAPIA* IN BRACKISH WATER MICROCOSM

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Abstract

The present study was conducted on the toxicity of ethoprophos to sexually mature red hybrid *Tilapia*. The NOEC and LOEC were 1 and 4 mg/L of ethoprophos; the 24-h LC_{50} and LC_{95} values were 8.41 and 21.00 mg/L. Bioconcentration of the insecticide from NOEC and LOEC in the surrounding water by the fish peaked (3.25 " 0.412 and 12.50 " 1.831 µg/g, respectively) eight to twelve hours after exposure. Bioconcentration from LOEC was 3.8-fold greater than at NOEC. The contaminated fish (after 24-h exposure to LOEC) eliminated 83 % of the ethoprophos residues within 12-h exposure to uncontaminated water. The order of partitioning of ethoprophos in the different tissues of the fish was gonads > liver> gut > gills > skin-muscle-bone.

1. INTRODUCTION

Widespread use of insecticides in Jamaica has contaminated its surface, ground and coastal waters, and aquatic fauna [1]. Studies on the fate of two widely used insecticides, endosulfan [2] and ethoprophos [3] revealed that up to 30% of the residues may run-off from mountainous slopes in the watershed with frequent rainfall, causing undetermined ecotoxic effects. In fact, a rapid survey of major rivers in Jamaica revealed the presence of ethoprophos in at least two of these rivers [4]. The present study was, therefore, conducted to determine the toxicity to and bioconcentration and tissue partitioning of ethoprophos in the fish *Tilapia*.

2. MATERIALS AND METHODS

Sexually mature red hybrid tilapia (*T. mossambica* x *T. nilotica*), 10 - 13 cm long, were obtained from a commercial fish farm and acclimatized to brackish water by exposing them to water of 0.25 and 0.5% salinity for five days each in the laboratory. The acclimatized fish were exposed to different concentrations of ethoprophos (Mocap10G) for 24 or 72 hr in aquaria with 15 L of brackish water at 0.5% salinity or 15% sea water and estuarine sediment and algae. The water was constantly aerated and food was provided daily. Each experiment had three replicates of 15 fish each.

Non-observable (NOEC), least observable (NOEC) and acute toxic effects were studied by exposing the fish 1, 4.0, 5.5, 7.0, 8.5 and 10.0 mg/L of ethoprophos. Toxic symptoms (darting, shuddering, sideswimming and death) were recorded every 8 hr for a 24-hour period. Probit analysis was used to determine the different toxicity levels.

Uptake was studied by exposing the fish to 1 mg/L or 4 mg/L of insecticide. At regular intervals, two fish were removed from each replicate, rinsed in distilled water twice, dried with paper towels, weighed and frozen for residue extraction. Elimination and tissue partitioning of residues were conducted by exposing two sets of fish to 4 mg/L of ethoprophos for 24 hr. One set of fish were dissected to separate the gut, gills, gonads, liver and skin-muscle-bone while the other was exposed to uncontaminated water for 72 hr for studying elimination of the residues. At regular intervals, two fish from each of the three replicates were removed, weighed and frozen as described earlier.

Frozen fish or tissue samples were thawed and homogenized in petroleum ether. Residues were partitioned in acetonitrile and cleaned using florisil according to the method described by Robinson and Mansingh [5]. Residues were determined by a Shimadzu 9A gas chromatograph equipped with a FPD. Analytical conditions were: glass column, 1.6 m by 2 mm packed with OV-17; carrier gas, nitrogen, at a flow rate of 30 - 35 mL/min; temperature settings: column 250EC, injector and detector 280EC. Detection levels ranged from 0.001 - 0.002 ng, recovery ranged from 75.8 - 80.4% from homogenized fish tissue and 89.2 - 91.7% from water. The reproducibility of results was 95.5 " 1.5%.

3. RESULTS AND DISCUSSION

The NOEC (no observable effect concentration), LOEC (least observable effect concentration), LATEC (least acute toxic effect concentration), LC_{10}, LC_{50} and LC_{95} of ethoprophos against the fish *Tilapia* are presented in Table 1. The LC_{50} values are well within the range of 0.27 - 13.8 mg/L reported by [6, 7] for different species of fish and suggests relatively low toxicity of ethroprophos to *Tilapia* when compared with other insecticides.

TABLE I. TWENTY FOUR HOUR NOEC, LOEC, LATEC, MATEC AND ATEC VALUES OF ETHOPROPHOS TO TILAPIA FISH

Toxicity concentration	Concentration (mg/L)	Fiducial limit	Slope	Proposed toxicity terminology
NOEC	1 - 2	-	-	NOTEC
LOEC	3 - 4	-	-	LOTEC
LC_{10}	4.13	2.410 - 5.202	4.141 " 0.934	LATEC
LC_{50}	8.41	7.205 - 10.232	4.141 " 0.934	MATEC
LC_{95}	21.00	15.072 - 47.518	4.141 " 0.934	ATEC

It may be pointed out that the difference between LOEC and LC_{10} is much less than between NOEC and LOEC or LC_{10} and LC_{50}. This may be attributed to the short experimental period of 24 hours for evaluating sublethal toxic effects. Furthermore, it is difficult to define NOEC and LOEC because (1) the toxicity of an insecticide is dependent upon the chemical properties of the insecticide and genetic heterogeneity of the target population, (2) the threshold of toxicity may not be behaviorally noticeable, (3) the toxic symptoms may be mild or pronounced, but recoverable, (4) these symptoms may be manifested by a few or more than half of the individuals in a population, (5) the symptoms may be abolished after a short or long period and (6) a few (< 10%) individuals may succumb after manifestation of pronounced toxic effects. How can all these effects be caused by a single LOEC?

It is, therefore, proposed that chronic and lethal or acute toxicities, and the concentrations causing such effects, be classified as NOTEC or no observable toxic effect (on 90% of the individuals) concentration, LOTEC or least observable mild and recoverable toxic effect (on < 50% of the individuals) concentration, MOTEC or mild, observable and recoverable toxic effect (on > 50% of the individuals) concentration, POTEC or pronounced observable and recoverable toxic effect (on > 25% of the individuals) concentration, LATEC or least acute toxic effect concentration (LC_{10}), MATEC or median acute toxic effect concentration (LC_{50}) and ATEC or acute toxic effect concentration (LC_{95}). The quantitative and arbitrary LOEC in Table 1 includes MOTEC and POTEC as well.

The uptake of ethoprophos was significantly ($P < 0.001$) faster and higher from LOEC than from NOEC (Fig.1). The rate of accumulation was most rapid during the first hour of exposure to both concentrations. Thereafter, at NOEC, it increased gradually to 3.25 " 0.72 Fg/g at 8 hr and fluctuated insignificantly ($P > 0.05$) for the next 64 hr. At LOEC, however, bioaccumulation continued to be steep for 4 hr (10.4 " 1.39 Fg/g) but gradual for the next 16 hr when the bioconcentration reached 12.5 " 2.41

Fg/g and fluctuated insignificantly ($P > 0.05$) afterwards. The bioconcentration factor (BCF) of ethoprophos in the fish was 2.4, and is a reflection of its high water solubility in water [8].

Fish, transferred to uncontaminated water after 24 hr. of exposure to LOEC, eliminated 82% of the initial concentration of ethoprophos in the first 12 hours, and a further 4% during the next 60 hours (Fig. 1). This rapid rate of elimination of the insecticide may be attributed to its high water solubility and its rapid transportation to gills and kidneys, as suggested by Tooby and Durbin's [9] for highly soluble insecticides.

The partitioning of ethoprophos was highest in the gonads > liver > gut > gills > skin, muscles and bones (Fig. 2). Gonads do bioconcentrate high levels of residues due to high lipid content [10] and are, therefore, adversely affected by the toxicants which is manifested in low fecundity [11, 12]. Accumulation in liver exposes the residues to detoxification [13], while those in gut and gills can be eliminated fairly fast.

The low BCF of ethoprophos, which is well below the critical value of 100 [14], and the rapid elimination of the accumulated residues by *Tilapia*, suggest that the insecticide may pose only limited danger to the fish, particularly since the LOEC levels are unlikely to be reached in the environment.

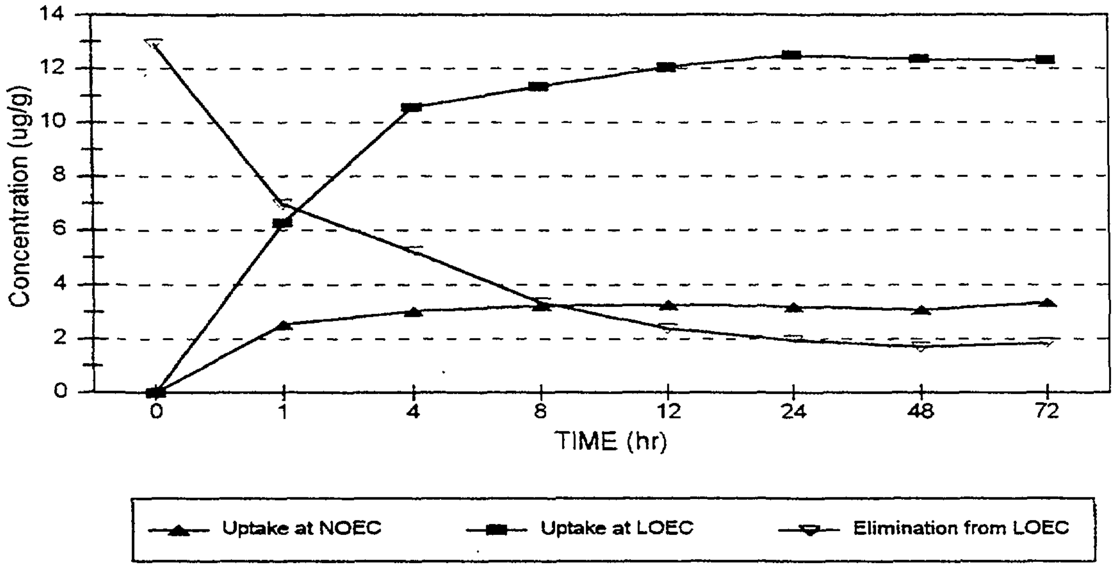

FIG. 1:Bioaccumulation of ethoprophos by hybrid Tilapia from non-observable and least-observable toxic effect concentration and elimination from whole body after 24 hr of exposure to least-observable toxic effect concentration under steady state conditions.

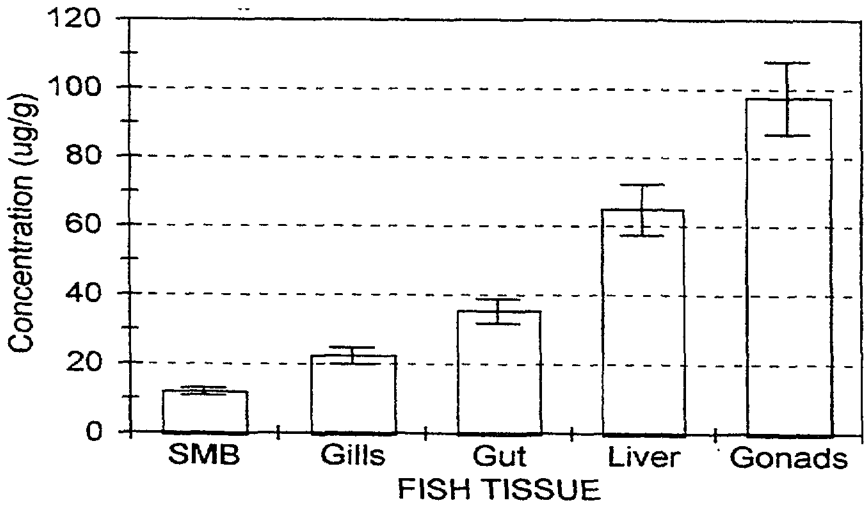

FIG. 2:The partitioning of accumulated ethoprophos in body tissues of hybrid Tilapia after 24 hr of exposure to least observable toxic effect concentration

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LAGOON SEDIMENT RADIOACTIVITY IN POLYNESIAN FRENCH NUCLEAR TEST SITES

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Abstract

In 1996, at the request of the French government, IAEA conducted an international study to assess the radiological situation of the atolls of Mururoa and Fangataufa. Results obtained by French scientists in the previous years were provided for the study. In this paper, some new results, such as ^{240}Pu/^{239}Pu activity ratio, are reported. 27 top-layer sediments were sampled in 1993 and 1995 in Mururoa and Fangataufa lagoons. Radioactivity measurements of the major man-made γ-emitters (^{60}Co, ^{125}Sb, ^{137}Cs and ^{155}Eu), of ^{90}Sr, ^{99}Tc and ^{239}Pu, together with activity ratios (^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu, ^{241}Am/^{239}Pu and ^{237}Np/^{241}Am) are given. These results are compared with previous measurements, in particular the radiological situations established in years 1984-90. Radiological maps, ^{155}Eu concentration, ^{239,240}Pu concentration and ^{238}Pu/^{239,240}Pu activity ratio, for sediment radioactivity in Mururoa and Fangataufa lagoons are shown. Results of two cores sampled in 1996 during the IAEA study are also reported. An assessment of total inventories is given for both atolls.

1. INTRODUCTON

Mururoa and Fangataufa atolls, in French Polynesia, were selected for atmospheric testing from 1966 to 1974) and underground testing (from 1975 to 1996) [1]. In these atolls, man-made radioactivity essentially results from the four barge tests which took place in 1966 and 1967, a few metres above the lagoon surface, and from safety tests.

Three barge experiments were conducted at Mururoa, in the western zone of the atoll (Dindon) for *Sirius* and *Aldebaran* and in the northern zone (Denise) for *Arcturus*. The fourth barge test, *Rigel*, was experimented in the central south eastern zone (Frégate) of Fangataufa. Due to the low elevation of the firing point, the fireball interacted with the lagoon bottom (at a depth of about 40 metres), resulting in deposits of fissile material and fission or activation products in the sediments.

In the 37 other atmospheric tests, the device was suspended from a balloon above the lagoon in the same zones. Their effects on the near environment were considerably reduced because of the increased firing point elevation (several hundred metres) which eliminated major interactions between the fireball and the lagoon.

During the same period, safety experiments conducted on the coral bedrock in the north of the Mururoa atoll, near the Denise zone, resulted in a localised deposit of plutonium on the ground and in the lagoon. These tests did not generate any nuclear energy, therefore no fission or activation products were created. After each test, radioactive contaminants deposit on the ground was either removed or sealed off by asphalting. The affected terrestrial zones were cleaned up from 1981 to 1987. Today, remaining products are essentially located in a sand bank (Colette bank) bordering the former safety experiment zone.

From 1975 to 1996, the testing was performed underground, therefore no significant radioactivity has been added to lagoon sediments.

2. SEDIMENTS SAMPLING AND RESULTS

27 top-layer sediments (the five top centimetres) were sampled in 1993 and 1995 in Mururoa and Fangataufa lagoons (see Fig. 1 and 2 for sampling locations). Measurements have been carried out by α and γ spectrometries, β counting and by ICP-MS techniques. Results are reported in Tables I and II. Lagoon sediment radioactivity is found mainly at the four locations mentioned above. Man-made radioactivity in the sediments is essentially due to ^{239}Pu. The other radionuclides detected, as listed in order of decreasing radioactivity in top-layer sediments, are ^{238}Pu, ^{240}Pu, ^{155}Eu, ^{241}Am, ^{60}Co and ^{137}Cs.

TABLE I. RADIONUCLIDE CONCENTRATIONS AND ACTIVITY RATIOS IN MURUROA TOP-LAYER SEDIMENTS SAMPLED IN 1993 [M93] AND 1995 [M95]

Location code	^{60}Co (Bq/kg d.w.)	^{90}Sr (Bq/kg d.w.)	^{99}Tc (Bq/kg d.w.)	^{125}Sb (Bq/kg d.w.)	^{137}Cs (Bq/kg d.w.)	^{155}Eu (Bq/kg d.w.)
M93 / G 09	1.122 ± 0.083	≤ 9.4	≤ 0.30	≤ 0.20	0.176 ± 0.048	22.7 ± 1.9
M93 / J 32	0.157 ± 0.027	≤ 3.3	≤ 0.20	≤ 0.21	≤ 0.041	2.58 ± 0.17
M93 / L 22	≤ 0.12	≤ 3.3	≤ 0.20	≤ 0.42	≤ 0.075	0.97 ± 0.19
M93 / P 27	0.230 ± 0.042	no measurement	≤ 0.40	≤ 0.36	≤ 0.063	1.68 ± 0.18
M93 / S 15	0.383 ± 0.040	no measurement	≤ 0.40	≤ 0.24	≤ 0.063	3.25 ± 0.21
M93 / U 24	0.839 ± 0.070	≤ 3.3	≤ 0.10	≤ 0.21	≤ 0.060	6.07 ± 0.30
M93 / Z 24	0.126 ± 0.032	≤ 8.6	≤ 0.30	≤ 0.30	≤ 0.055	1.32 ± 0.15
M93 / Z 26	0.125 ± 0.038	≤ 3.4	≤ 0.20	≤ 0.29	≤ 0.055	1.05 ± 0.15
M95 / A 06	≤ 0.074	≤ 3.5	≤ 0.020	≤ 0.23	≤ 0.076	1.11 ± 0.14
M95 / G 05	1.17 ± 0.10	≤ 16	≤ 0.050	≤ 0.25	0.312 ± 0.051	7.80 ± 0.57
M95 / J 32	0.278 ± 0.043	≤ 3.7	≤ 0.020	≤ 0.24	≤ 0.082	1.75 ± 0.16
M95 / L 32	0.594 ± 0.077	≤ 14	≤ 0.025	≤ 0.35	≤ 0.13	5.32 ± 0.42
M95 / O 41	0.706 ± 0.068	≤ 19	≤ 0.028	≤ 0.30	≤ 0.11	5.39 ± 0.43
M95 / P 27	1.60 ± 0.13	≤ 3.0	≤ 0.020	≤ 0.29	≤ 0.11	2.09 ± 0.20
M95 / S 15	0.275 ± 0.038	≤ 3.6	≤ 0.020	≤ 0.23	≤ 0.082	1.19 ± 0.14
M95 / U 24	0.144 ± 0.035	≤ 3.5	≤ 0.020	≤ 0.25	≤ 0.084	1.49 ± 0.17
M95 / Z 25	0.337 ± 0.043	≤ 3.2	≤ 0.020	≤ 0.24	≤ 0.082	2.57 ± 0.23

Location code	^{239}Pu (Bq/kg d.w.)	^{238}Pu/^{239}Pu activity ratio	^{240}Pu/^{239}Pu activity ratio	^{241}Am/^{239}Pu activity ratio	^{237}Np/^{241}Am activity ratio
M93 / G 09	109 ± 9	0.286 ± 0.041	0.181 ± 0.023	0.098 ± 0.013	0.0030 ± 0.0010
M93 / J 32	21.1 ± 1.7	0.158 ± 0.023	0.123 ± 0.015	0.063 ± 0.016	0.0026 ± 0.0018
M93 / L 22	10.9 ± 0.9	0.275 ± 0.042	0.150 ± 0.024	0.091 ± 0.022	≤ 0.0056
M93 / P 27	23.4 ± 2.0	0.256 ± 0.036	0.118 ± 0.017	0.054 ± 0.009	≤ 0.0030
M93 / S 15	26.2 ± 2.0	0.277 ± 0.038	0.119 ± 0.018	0.067 ± 0.008	0.0029 ± 0.0019
M93 / U 24	74.6 ± 5.9	0.271 ± 0.036	0.118 ± 0.013	0.044 ± 0.005	0.0023 ± 0.0013
M93 / Z 24	14.3 ± 1.2	0.271 ± 0.043	0.125 ± 0.019	0.049 ± 0.011	0.0046 ± 0.0017
M93 / Z 26	7.52 ± 0.60	0.113 ± 0.026	0.114 ± 0.015	0.076 ± 0.021	≤ 0.017
M95 / A 06	9.04 ± 0.68	0.221 ± 0.040	0.152 ± 0.023	0.111 ± 0.019	≤ 0.013
M95 / G 05	96.3 ± 3.7	0.145 ± 0.030	0.136 ± 0.028	0.063 ± 0.005	0.0013 ± 0.0005
M95 / J 32	25.1 ± 3.8	0.113 ± 0.030	0.102 ± 0.030	0.065 ± 0.012	≤ 0.0077
M95 / L 32	69.9 ± 4.7	0.237 ± 0.046	0.133 ± 0.021	0.100 ± 0.011	0.0011 ± 0.0003
M95 / O 41	143 ± 7	0.283 ± 0.052	0.104 ± 0.041	0.152 ± 0.013	0.00014 ± 0.00004
M95 / P 27	17.0 ± 1.0	0.288 ± 0.061	0.109 ± 0.012	0.055 ± 0.011	≤ 0.012
M95 / S 15	9.4 ± 1.2	0.277 ± 0.084	0.110 ± 0.030	0.095 ± 0.020	0.0040 ± 0.0019
M95 / U 24	17.1 ± 1.9	0.281 ± 0.071	0.107 ± 0.020	0.078 ± 0.015	0.0026 ± 0.0011
M95 / Z 25	40.9 ± 0.7	0.203 ± 0.025	0.119 ± 0.010	0.042 ± 0.005	0.0046 ± 0.0018

TABLE II. RADIONUCLIDE CONCENTRATIONS AND ACTIVITY RATIOS IN FANGATAUFA TOP-LAYER SEDIMENTS SAMPLED IN 1993 [F93] AND 1995 [F95]

Location code	^{60}Co (Bq/kg d.w.)	^{90}Sr (Bq/kg d.w.)	^{99}Tc (Bq/kg d.w.)	^{125}Sb (Bq/kg d.w.)	^{137}Cs (Bq/kg d.w.)	^{155}Eu (Bq/kg d.w.)
F93 / Pass	0.303 ± 0.038	≤ 3.3	≤ 0.40	≤ 0.18	≤ 0.073	2.76 ± 0.20
F93 / Pavi	0.881 ± 0.057	≤ 3.3	≤ 0.40	≤ 0.14	≤ 0.038	1.12 ± 0.13
F93 / Cata	2.22 ± 0.13	≤ 3.5	≤ 0.30	≤ 0.24	0.118 ± 0.042	8.16 ± 0.39
F93 / Echo	3.55 ± 0.19	≤ 8.0	≤ 0.40	≤ 0.16	0.161 ± 0.053	15.5 ± 1.0
F93 / Term	1.76 ± 0.10	≤ 3.8	≤ 0.20	≤ 0.19	≤ 0.062	7.87 ± 0.37
F95 / C 27	0.571 ± 0.066	≤ 3.4	≤ 0.020	≤ 0.25	≤ 0.094	0.57 ± 0.11
F95 / L 35	0.151 ± 0.029	≤ 3.6	≤ 0.020	≤ 0.15	≤ 0.056	0.70 ± 0.10
F95 / M 09	2.72 ± 0.20	≤ 17	≤ 0.020	≤ 0.26	0.122 ± 0.046	7.65 ± 0.57
F95 / M 26	2.52 ± 0.20	≤ 16	≤ 0.058	≤ 0.41	0.339 ± 0.067	11.5 ± 1.0
F95 / T 13	3.97 ± 0.28	≤ 17	≤ 0.020	≤ 0.25	0.176 ± 0.051	12.4 ± 1.0

Location code	^{239}Pu (Bq/kg d.w.)	^{238}Pu/^{239}Pu activity ratio	^{240}Pu/^{239}Pu activity ratio	^{241}Am/^{239}Pu activity ratio	^{237}Np/^{241}Am activity ratio
F93 / Pass	22.7 ± 1.9	0.467 ± 0.069	0.190 ± 0.037	0.079 ± 0.011	≤ 0.0021
F93 / Pavi	8.86 ± 0.70	0.391 ± 0.061	0.177 ± 0.034	0.080 ± 0.015	≤ 0.0068
F93 / Cata	58.3 ± 4.5	0.487 ± 0.074	0.182 ± 0.022	0.096 ± 0.010	0.00072 ± 0.00029
F93 / Echo	125 ± 9	0.398 ± 0.049	0.185 ± 0.022	0.080 ± 0.007	0.00082 ± 0.00019
F93 / Term	63.5 ± 5.0	0.351 ± 0.051	0.181 ± 0.022	0.075 ± 0.008	0.00143 ± 0.00041
F95 / C 27	7.04 ± 0.56	0.366 ± 0.072	0.178 ± 0.024	0.108 ± 0.030	≤ 0.0054
F95 / L 35	9.72 ± 0.41	0.472 ± 0.098	0.171 ± 0.048	0.063 ± 0.011	≤ 0.014
F95 / M 09	70.6 ± 9.0	0.416 ± 0.098	0.160 ± 0.068	0.093 ± 0.014	0.00119 ± 0.00034
F95 / M 26	111 ± 7	0.448 ± 0.063	0.184 ± 0.021	0.094 ± 0.011	0.00076 ± 0.00032
F95 / T 13	160 ± 15	0.422 ± 0.079	0.188 ± 0.027	0.066 ± 0.009	0.00095 ± 0.00030

Fig. 1 and Fig. 2 show ^{155}Eu concentration, ^{239,240}Pu concentration and ^{238}Pu/^{239,240}Pu activity ratio in Mururoa and Fangataufa top-layer sediments. The radiological maps presented here were based on the results of sampling campaigns undertaken from 1984 to 1990 in these zones [2]. More than one hundred top-layer sediments were sampled in each of the locations mentioned above. They were supplemented by cores, including some down to 5 metres depth, to plot the vertical profile of radioactivity concentration in the sediments. Outside these locations, about five hundred top layer sediments, supplemented by cores, were also sampled. Concentrations measured in 1993-95 samples are in good agreement with the previous radiological situation. Concentration levels are similar for both atolls.

Depending on the location, ^{239}Pu concentration in top-layer sediments ranges between 7 and 160 Bq/kg. Of course, higher concentrations may be observed near barge or safety test zones. ^{239,240}Pu concentration in top-layer may reach 2.0×10^4 Bq/kg in Dindon zone, 6.5×10^3 Bq/kg in Denise zone, 2.5×10^6 Bq/kg near the safety test zone and 2.0×10^4 Bq/kg in Frégate zone. Sediments near the passes and the *hoa*[1] (South West of Mururoa and West of Fangataufa) show concentration levels under 20 Bq/kg. ^{240}Pu/^{239}Pu activity ratio ranges between 0.10 and 0.18 in Mururoa. This activity ratio is stable at 0.18 in Fangataufa (only one barge test).

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[1] Tahitian name for little channel allowing the ocean and lagoon waters to mingle. The *hoa* delimit emerged islets called *motu*.

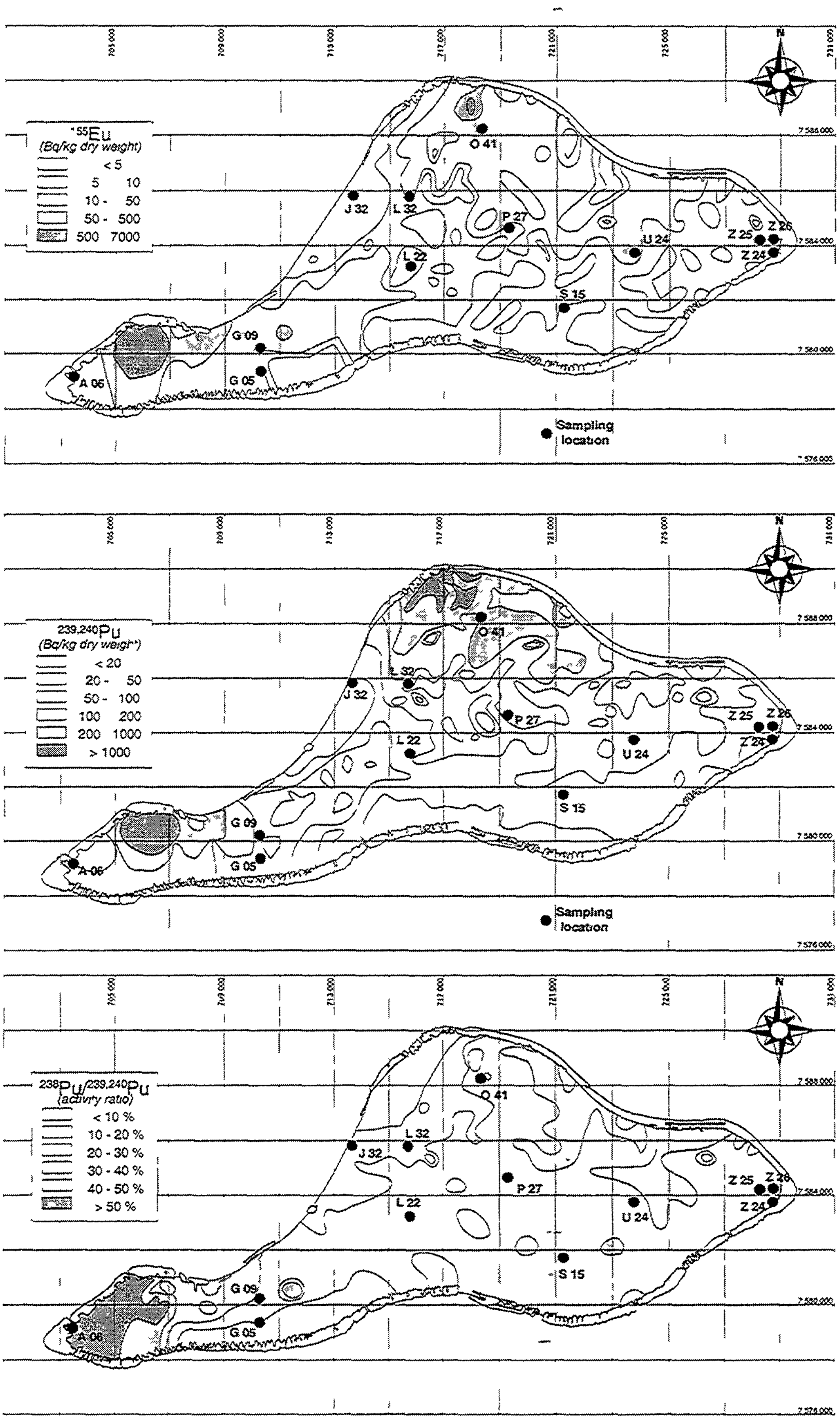

FIG 1 ^{155}Eu concentration, $^{239\,240}$Pu concentration and ^{238}Pu/$^{239\,240}$Pu activity ratio in Mururoa top-layer sediments (on 01/04/1988) and 1993-95 sampling locations

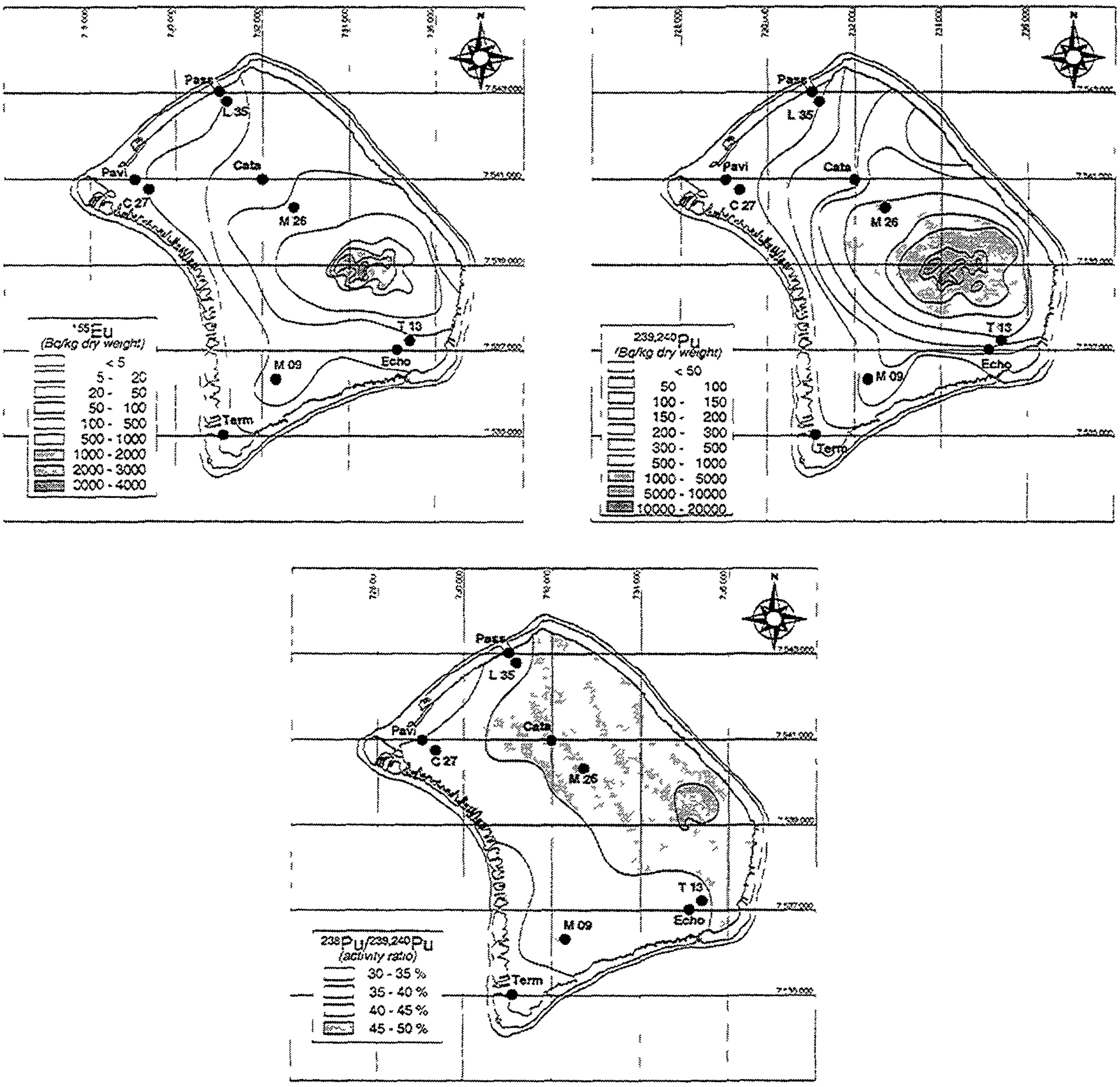

FIG 2. ^{155}Eu concentration, ^{239,240}Pu concentration and ^{238}Pu/^{239,240}Pu activity ratio in Fangataufa top-layer sediments (on 01/09/1987) and 1993-95 sampling locations.

The ^{238}Pu/^{239}Pu activity ratio ranges between 0.3 and 0.5 (effect of *Rigel* test) in Fangataufa. In Mururoa, this ratio varies from 0.1 to 0.3. Ratios below 0.01 may be seen in the Northern zone (effect of safety tests) and close to 0.6 in the Western zone (effect of *Sirius* test). The ^{241}Am/^{239}Pu activity ratio varies from 0.04 to 0.15 for both atolls. The ^{237}Np/^{241}Am activity ratios are low, below 0.005.

Activation and fission products concentrations are lower than those of actinides. ^{60}Co and ^{155}Eu are still detected, but their concentrations, between 0.6 and 23 Bq/kg for ^{155}Eu and between 0.1 and 4 for ^{60}Co, are decreasing according to their half-life. ^{137}Cs concentrations are slightly lower in top-layer sediments and not always detected. The higher detection limits for the ^{90}Sr explained partly why it is not detected. But previous measurements, made near the hot spots of the barge test, show concentration levels of ^{90}Sr in top-layer sediment of the same order of magnitude than those of ^{137}Cs.

The total radioactivity of man-made radionuclides on the lagoon bed was determined from core sample campaign carried out between 1984 and 1990. Results of two cores sampled in 1996 during the study of the radiological situation at both atolls by IAEA [3] are given in Table III. These cores were sampled in hot spots of two barge tests, *Rigel* at Fangataufa and *Sirius* at Mururoa. At the former test points, radioactivity is distributed vertically over a few metres. In the *Sirius* impact zone for example, the maximum radioactivity level in sediment is found between 0.5 and 2.5 m. Below 3.5 m, radioactivity drops to less than 1 000 Bq/kg [2]. The profiles are similar for all radionuclides with a slight difference for ^{137}Cs an ^{90}Sr. This is due to the easier dissolution of caesium and strontium, respectively chemical analogous of potassium, sodium and calcium.

TABLE III. CONCENTRATIONS IN TWO CORE SEDIMENTS SAMPLED IN 1996

Depth (cm)	^{60}Co (Bq/kg d.w.)	^{90}Sr (Bq/kg d.w.)	^{137}Cs (Bq/kg d.w.)	^{155}Eu (Bq/kg d.w.)	^{238}Pu (Bq/kg d.w.)	^{239,240}Pu (Bq/kg d.w.)	^{241}Am (Bq/kg d.w.)
RIGEL TEST ZONE							
0 - 10	174 ± 14	430 ± 90	138 ± 11	261 ± 20	1160 ± 150	2 950 ± 360	254 ± 20
10 - 25	34.3 ± 2.8	342 ± 72	87.0 ± 7.0	67.5 ± 5.5	317 ± 39	810 ± 99	63.8 ± 5.5
25 - 44	41.2 ± 2.7	270 ± 58	150 ± 93	62.0 ± 4.0	282 ± 37	709 ± 90	63.1 ± 4.7
44 - 63	50.8 ± 4.1	251 ± 54	287 ± 22	93.3 ± 7.7	525 ± 71	1 350 ± 180	83.7 ± 7.0
63 - 96	418 ± 33	700 ± 150	546 ± 43	673 ± 52	3 000 ± 370	7 640 ± 940	663 ± 52
SIRIUS TEST ZONE							
0 - 8	132 ± 12	580 ± 120	451 ± 40	675 ± 58	1 790 ± 280	3 540 ± 550	494 ± 43
8 - 16	754 ± 66	540 ± 120	879 ± 77	2 110 ± 180	5 240 ± 710	9 780 ± 1 330	1 520 ± 130
16 - 20	278 ± 19	570 ± 120	246 ± 17	902 ± 59	1 940 ± 220	3 680 ± 420	659 ± 43
20 - 29	1 340 ± 100	840 ± 180	623 ± 48	3 900 ± 310	11 700 ± 1 700	21 400 ± 3 100	2 800 ± 220
29 - 37	279 ± 22	no measurement	401 ± 31	505 ± 39	no measurement	no measurement	372 ± 29
37 - 50	735 ± 25	1 970 ± 400	583 ± 21	1 400 ± 130	3 760 ± 530	7 380 ± 1 030	1 040 ± 100
50 - 80	2 550 ± 210	no measurement	1 770 ± 140	4 060 ± 330	no measurement	no measurement	3 020 ± 240
80 - 83	2 000 ± 170	no measurement	2 040 ± 180	2 820 ± 240	no measurement	no measurement	2 110 ± 210
83 - 104	2 650 ± 210	13 200 ± 2 700	3 000 ± 240	3 640 ± 290	8 410 ± 1 080	16 300 ± 2 100	2 780 ± 220
104 - 125	2 270 ± 180	no measurement	3 650 ± 290	3 180 ± 260	no measurement	no measurement	2 430 ± 200
125 - 167	2 050 ± 120	no measurement	4 480 ± 270	2 920 ± 170	no measurement	no measurement	2 150 ± 130
167 - 212	1 790 ± 150	11 800 ± 2 400	4 710 ± 380	2 780 ± 230	6 040 ± 600	12 100 ± 1 200	2 010 ± 160

The assessment of the man-made radionuclide presence in the sediments is given in Table IV. This assessment is given on the strict basis of radionuclide half-lives, disregarding the fraction which has gone into solution since the date of sampling. Inventory estimated by IAEA during the international study [3] are also reported. As can be seen, the estimations are consistent. The total ^{239}Pu inventory for both atolls is about 22 TBq (near 10 kg of ^{239}Pu). Activation and fission product inventories are in the order of 4 TBq, near 7 times lower than that of ^{239}Pu. For comparison, the inventory of the naturally occurring isotope ^{40}K in the Mururoa lagoon water is 56 TBq.

TABLE IV. TOTAL INVENTORY (TBq) IN SEDIMENT (REFERENCE DATE 01/01/1997).

	MURUROA			FANGATAUFA	
Radionuclide	Centre lagoon (IAEA Study)	Centre lagoon (French data)	Total lagoon (French data)	Total lagoon (IAEA Study)	Total lagoon (French data)
^{60}Co	0.02	0.04	0.4	0.1	0.03
^{90}Sr	no value	negligible	1.1	no value	0.3
^{125}Sb	no value	negligible	0.02	no value	0.004
^{137}Cs	0.02	negligible	0.8	0.05	0.2
^{155}Eu	0.07	0.08	0.7	0.3	0.4
^{238}Pu	0.3	0.6	3.3	2.3	2.9
^{239}Pu+^{240}Pu	1.8	3.6	15.8* + 2.2**	5.5	6.1* + 1.3**
^{241}Am	0.04	0.2	0.8	0.3	0.4

** : ^{239}Pu* *** : ^{240}Pu*

These radionuclide inventories in lagoons are lower than those reported for Bikini or Enewetak. The ^{239,240}Pu inventories to a depth of 16 cm in the sediment column are estimated to be 54 TBq at Bikini and 44 TBq at Enewetak [4]. The ^{239,240}Pu total inventory in the Bikini lagoon is estimated of order of 120 TBq [5][6], that is near seven times the Mururoa inventory. In comparison with non nuclear test sites, the ^{239,240}Pu inventory at French test sites is slightly larger than that of the Kara Sea, 13 TBq, and is lower than the inventory of the upper 30 cm of the Irish Sea, 280 TBq [7] (an estimated total activity of 610 TBq of ^{239,240}Pu has been discharged to the Irish Sea during the period 1952-94 [8]).

For ^{60}Co and ^{137}Cs, Bikini inventories in the top four centimetres were respectively 0.74 TBq and 1.7 TBq on June 1979 [9], twenty one years after the last atmospheric tests in this atoll. These quantities are estimated to be less than 35% of the total inventory in the sediment column. Total inventories for the Mururoa lagoon are much lower, respectively 0.4 TBq and 0.8 TBq, more than 30 years after the latest barge test. In comparison, the ^{137}Cs and ^{90}Sr inventories of the Kara Sea are higher, 1 100 and 1 000 TBq [7].

The exchange processes taking place between the sediments and the sea water were studied previously in laboratory and in situ (extraction of interstitial water in contact with the sediment) [10]. According to location, plutonium distribution coefficients (K_d) for the Mururoa lagoon vary widely in a range from a few 10^3 to a few 10^5. These values are consistent with data published on different types of sediment and with the IAEA recommended values (10^4 to 10^6).

In a previous work [10], we reported an approximate 20 GBq of plutonium flushed out to sea yearly through the Mururoa pass. This value was higher than that estimated by IAEA [3], 6.4 GBq/a (4.6 GBq/a for Fangataufa). This is due to a different value taken for the average turn-over time of water in the lagoon[2], one month instead of three months for IAEA. By comparison, the discharge of ^{239,240}Pu from Bikini and Enewetak atolls is 120 GBq/a and 100 GBq/a, respectively [11]. For ^{90}Sr and ^{137}Cs, the IAEA estimated release rates from the Mururoa and the Fangataufa lagoons are 18 GBq/a and 8.6 GBq/a of ^{90}Sr, 5.7 GBq/a and 5.3 GBq/a of ^{137}Cs respectively.

3. CONCLUSION

As only four barge tests were carried out in Mururoa and Fangataufa, man-made radionuclides inventories in lagoons are lower than those reported for nuclear test sites in the Marshall Islands. The ^{239,240}Pu total inventory in the Bikini lagoon is estimated to be near seven times that of Mururoa. In comparison with non nuclear test sites, the ^{239,240}Pu inventory at French test sites is slightly larger than that of the Kara Sea and much lower than that of upper sediments of the Irish Sea.

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THE PRODUCTION AND DISSOLUTION OF NUCLEAR EXPLOSIVE MELT GLASSES AT UNDERGROUND TEST SITES IN THE PACIFIC REGION*

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Abstract

From 1975 to 1996 the French detonated 140 underground nuclear explosions beneath the atolls of Mururoa and Fangataufa in the South Pacific; from 1965 to 1971 the United States detonated three high yield nuclear tests beneath Amchitka Island in the Aleutian chain. Approximately 800 metric tons of basalt is melted per kiloton of nuclear yield; almost 10^7 metric tons of basalt were melted in these tests. Long-lived and toxic radionuclides are partitioned into the melt glass at the time of explosion and are released by dissolution with seawater under saturated conditions. A glass dissolution model predicts that nuclear melt glasses at these sites will dissolve in 10^6 to 10^7 years.

1. INTRODUCTION

Due to the relative isolation of volcanic islands in the Pacific region, the French Commissariat à l'Energie Atomique and United States Atomic Energy Commission conducted a series underground nuclear tests on Pacific islands during the period 1965 to 1996. The United States conducted three approximate megaton yield nuclear explosions underground at Amchitka Island in the Aleutian island-arc chain and the French conducted 140 lower yield underground nuclear explosions beneath the atolls of Mururoa and Fangataufa in French Polynesia. All of the tests were conducted in basaltic rocks at depths of burial beneath sea-level. While the detonation of nuclear explosives underground allows for the containment of nearly all prompt radiation residual from the explosion, the subsequent long-term dissolution of radioactive melt glass poses a potential threat to the marine environment. Recently there has been international concern about the potential for radionuclide migration at these sites. Accurate radiological assessments require an understanding of the thermal and mechanical effects of an underground nuclear explosion on submarine basalts, the production and post-shot distribution of radionuclides, the physical and chemical characteristics of the residual matrices, and their long-term performance under saturated conditions.

2. PHENOMENOLOGY

Phenomenology refers to the effects of a nuclear explosion on the surrounding geologic environment. Early-time phenomenology refers to physical and chemical processes that occur immediately after a nuclear detonation during the time the explosion cavity reaches it maximum dimension. Late-time phenomenology refers to thermally-induced process affecting the standing cavity which leads its eventual collapse. Tompson et al. [1] provide a comprehensive summary of phenomenology as it relates to the evolution of a nuclear explosion cavity and collapse chimney.

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2.1. Early-time phenomenology

When an underground nuclear explosion is detonated, sufficient energy is released to instantaneously vaporize rock adjacent to the firing point. Initial temperatures are several Million °K and pressures are close to 1 Mbar. A compressive, outwardly propagating shock wave is generated within a millisecond which crushes, melts, and vaporizes rock creating an expanding open volume or cavity. As the geologic media surround the explosion point is melted, pore water is also vaporized creating steam in the still growing cavity; CO_2 may also be produced from the fusion of carbonate materials. Depending on the explosive yield the cavity reaches its maximum size within 80 to 500 milliseconds. A compressive hoop stress is created by the rebound of the adjacent media; this residual stress will tend to close radial fractures that were created during the initial expansion of the cavity. The final size of the standing cavity is a function of the explosive yield, the density of the surround rock and the overburden stress. Based on underground experience, the French provide an empirical measure for maximum cavity dimension at Mururoa and Fangataufa:

$$R_c = 100\,(Y/h)^{1/3} \qquad (1)$$

where

R_c is the cavity radius in meters,
Y is the total yield in kilotons,
h is depth of device burial in meters.

2.2. Late-time phenomenology

After the shock waves and elastic stress waves have dissipated, less volatile vapors begin to condense on the walls of the standing cavity in a molten states. The melt follows down the walls of the cavity and drips from the roof forming a puddle on the cavity bottom. For basalts with an average density of 2.5 g/cm^3 the French report that approximately 800 metric tons of rock are melted per kiloton of nuclear yield [2]. Water vapor, noncondensible gases (such as CO_2 and H_2) and other noncondensed radionuclides (such as tritiated water vapor, ^{85}Kr, and ^{137}Xe) are still present as gases in the cavity. Within minutes to hours after the detonation, thermal energy in the gas is conductively transferred through the walls of the cavity to the surrounding geologic media creating high thermal gradients. These thermal stresses induce ablation and spall of wall rock which falls into the cavity quenching the melt.

Within minutes to hours debris continues to fill the cavity. Condensation of gas causes a reduction in cavity pressure until it reaches a few bars. When the pressure in the cavity drops below surrounding ambient lithostatic pressure, the cavity collapses and propagates upwards forming a collapse chimney. If the explosive yield is low, the rock strength is high, or the test is deeply buried, the collapse chimney will not reach the ground surface.

3. RADIONUCLIDE PRODUCTION AND DISTRIBUTION

For a generic thermonuclear device, the radioactivity residual from an underground nuclear is derived from five components:

(1) Residue of nuclear fuel materials (e.g.,^{3}H, ^{6}LiD, ^{235}U, ^{238}U, ^{239}Pu, ^{240}U),
(2) Reaction products of fuel materials (e.g., ^{3}H, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Am),
(3) Fission products (e.g., ^{85}Kr, ^{90}Sr, ^{99}Tc, ^{125}Sb, ^{129}I, ^{137}Cs, ^{155}Eu),
(4) Activation products on non-fuel device materials (e.g., ^{14}C, ^{60}Co, ^{55}Fe), and
(5) Activation products of backfill materials and adjacent geology (e.g., ^{36}Cl, ^{41}Ca, ^{152}Eu).

The production of selected radionuclides is presented in Table I.

TABLE I. PRODUCTION AND PARTITIONING (IN %) BETWEEN GLASS, DEBRIS RUBBLE, GAS AND WATER OF SELECTED RADIONUCLIDES PRODUCED DURING AN UNDERGROUND NUCLEAR EXPLOSION [3]

Nuclide	Decay	Half-Life (a)	Production	Glass	Rubble	Gas	Water
^{3}H	β^-	12.33	fuel residue and fuel product	0	0	2	98
^{14}C	β^-	5730	(n,p) in device	0	10	80	10
^{85}Kr	β^-	10.77	fission product	0	10	80	10
^{90}Sr	β^-	28.78	fission product	40	60	0	0
^{99}Tc	β^-	211100	fission product	80	20	0	0
^{129}I	β^-	15700000	fission product	50	40	0	10
^{137}Cs	β^-	30.07	fission product	40	60	0	0
^{152}Eu	EC	13.54	(n, γ) in environment	95	5	0	0
^{155}Eu	β^-	4.76	fission product	95	5	0	0
^{237}Np	α	2144000	fuel residue and fuel product	95	5	0	0
^{239}Pu	α	24110	fuel residue and fuel product	98	2	0	0
^{241}Am	α	432	fuel residue and fuel product	98	2	0	0

Refractory radionuclides with higher boiling points and lower vapor pressures (i.e., Zr, Tc, Ce, Eu, U, Pu, Am, Cm) are largely volumetrically incorporated in the puddle glass. Radionuclides with lower boiling points and higher vapor pressures (H, Sr, Ru, Sb, Cs, Ba) are heterogeneously distributed throughout the cavity-chimney system as a result of volatilization, displacement, and condensation accompanying cavity collapse. Volatile radionuclides will largely condense on fracture and mineral surfaces in addition to partitioning in the glass. The fractionation of radionuclides has also been documented on field-scale. Post-shot drilling into a nuclear test cavity-chimney have returned samples which provide a nearly continuous profile of radioactivity ascending from the cavity upwards through the collapse chimney [4]. Refractory radionuclides (e.g., ^{152}Eu, ^{154}Eu) are concentrated in the puddle glass while ^{3}H and volatile fission products (e.g., ^{137}Cs) are found in the higher chimney away from the working point. Table I shows the general partitioning of radionuclides (in %) between melt glass, crystalline rubble and breccia, water, and gas phases for selected radionuclides residual from underground nuclear tests.

4. GLASSES PRODUCED DURING AN UNDERGROUND NUCLEAR EXPLOSION

Nuclear explosive melt glass is produced from the condensation of vaporized rock, the shock melting of native rock, and the melting of neighboring rock in contact with the melt and vapor [5].

These glasses are significant for two reasons:

(1) Glasses volumetrically incorporate radionuclides which are subsequently released by matrix dissolution under saturated or partially saturated conditions.

(2) The nuclear explosive melt glasses partition actinide species (i.e., ^{235}U, ^{238}U, ^{237}Np, ^{239}Pu, ^{240}U) which have higher toxicities (organ dose conversion factors: ~10^{-6} to ~10^{-5} Sv/Bq) and half-lives sufficiently long to dominate the residual source term inventory after ~ 200 years (i.e., $t_{1/2}$ of ^{239}Pu is 2.41×10^4 years, $t_{1/2}$ of ^{237}Np is 2.14×10^6 years).

The glass produced during an underground nuclear explosion is extremely heterogeneous and includes:

(1) Dark, dense highly radioactive glass which is representative of the puddle accumulation of melt.
(2) Light, variably vesicular glass with less radioactivity which is representative of melted host rock.
(3) Globs, belbs, and coatings of dark glass which formed from the rapid condensation of vaporized silicates on fracture surfaces [6].

Autoradiographic and petrographic analyses of three samples of glass from a single test confirm the presence of a dark vesicular glass with a high alpha track density as well as a less vesicular lighter colored mixed glass with a lower fission track density [7]. The major and trace element composition of the glass mimics that of the host rock from which it both vaporized and melted [6]. In general, the melt glass is heterogeneous containing both mineral and lithic inclusions. Quenching is non-uniform. For these reasons, melt glass is both variably charged with fine vesicles and fractured.

4.1. Glass produced beneath Mururoa, Fangataufa, and Amchitka

The French have detonated 140 underground nuclear explosions (exclusive of safety trials) beneath the atolls of Mururoa and Fangataufa in French Polynesia during the period 1975 to 1996 [2]. The total yield of all the French underground tests is ~3,200 kilotons [3]. On the Aleutian Islands in the Bering Sea the United States detonated three high yield nuclear explosions: LONGSHOT on 29 October 1965 with a total yield of ~ 80 kilotons, MILROW on 2 October 1969 with a yield of ~ 1000 kilotons, and CANNIKIN on 6 November 1971 with a total yield < 5000 kilotons [8]. The firing medium for all these explosions was basalt produced by volcanism associated with the formation of ocean islands (hot spots and arcs). The SiO_2 concentration of basalt from the CANNIKIN emplacement hole is 44.2 weight % and the SiO_2 content of Mururoa basalts is 44.8 weight % SiO_2. The bulk density of the South Pacific and Amchitka basalts is 2.5 g/cm^3.

As noted above, for rocks of this density the French report 800 metric tons of basalt is melted per kiloton of total nuclear yield. Assuming a total yield for the French tests on Mururoa and Fangataufa of 3200 kilotons and a maximum (upper limit) total yield of United States nuclear tests on Amchitka of 6080 kilotons, 2.56×10^6 metric tons of melt glass is estimated to be beneath Mururoa and Fangataufa and 4.86×10^6 metric tons is estimated to be beneath Amchitka.

5. GLASS DISSOLUTION

Glasses are thermodynamically unstable matrices which transform with time to stable crystalline phases. Water acts as a flux to allow the transformation; the rate of the transformation provides an upper limit to release rates of radioactive elements contained in the glass. Glass reactions in aqueous environments begin with water diffusion into the glass and alkali ion exchange. Hydration and ion exchange on the glass surface result in an inner diffusion layer several microns thick where alkalis and water form distinct concentration gradients and an outer, hydrated gel layer where Si network dissolution occurs [9]. The layer migrates into the glass releasing elements stoichiometrically. Most of the element are quickly incorporated into alteration phases which include clays, zeolites, oxides, and hydroxides.

In general the dissolution of glass can be described by a rate equation which relates the dissolution of glass per unit time to a rate constant for dissolution, the reactive surface area of theglass and an affinity term that represents the thermodynamic driving force for dissolution of the solid phase. A simplified rate equation may be written:

$$dn/dt = S\,k\,(1-Q/K) \qquad (2)$$

where

n	is grams of glass released,
t	is the unit time,
S	is the reactive surface area,
k	is the forward rate constant for dissolution,
Q	is the concentration product for the dissolving solid in solution,
K	is the solubility product for the dissolving solid.

As species originally present in the glass builds up in solution, the dissolution rate decreases. Previous studies of silicate glasses have shown that higher concentrations of dissolved silica slows the reaction rate. Because of lack of more detailed information, a glass dissolution model has been developed that calculates only the release of silica from the matrix. A complete description of the model is provided by Tompson et al. [1]. The rate of dissolution of nuclear explosive melt glass may be calculated as a function of the temperature of reaction, the mass of glass dissolved, the SiO_2 content of the glass, the SiO_2 content of the reacting solution, the pH of the solution, the density of the glass, and the surface area of the glass. Using a temperature of 30°C, 45 weight % SiO_2 in the basalt, 10 mg/L Si in the reacting fluid, and a pH of 8.0, the model calculates a dissolution rate of 1.56×10^{-3} grams of glass/m^2/day. This rate compares favorably with dissolution rates (7.26×10^{-4} grams/m^2/day to 7.26×10^{-3} grams/m^2/day) obtained from experimental studies of the reaction of Mururoa basalts and free silicon seawater calculated at 25°C [10].

Using 8000 metric tons of glass produced for a 10 kiloton explosion, a melt glass porosity of 30%, and an empirically derived glass cracking factor of 25 which relates the total surface areas to the geometric surface area, the model calculates a melt glass surface area of 0.07 cm^2/g. The resulting final reaction rate for the glass is 9.3×10^1 g/day. For a 100 kiloton yield explosion, the final reaction rate will increase to 4.3×10^2 g/day. For a 1000 kiloton yield explosion, the rate rises to 2.0×10^3 g/day. Using the 10 kiloton rate (9.3×10^1 g/day) for the glass beneath Mururoa and Fangataufa, all the glass will dissolve in 7.5×10^7 years. Using the 1000 kiloton rate (2.0×10^3 g/day) for Amchitka, all the glass will dissolve in 6.7×10^6 years. The hydraulic conductivity of the Mururoa and Fangataufa massive basalts ranges between 10^{-8} and 10^{-7} m/sec facilitating glass-water reactions [11].

6. CONCLUSIONS

The above calculations apply only to the dissolution of melt glass. It should be emphasized that transport of radionuclides through the near-field involves a variety of process in addition to dissolution which may include ion-exchange, precipitation, complexation, sorption, and formation of or sorption to colloids [12]. As well, radionuclide concentrations will be dispersed and diluted by seawater. Over an interval of 10^6 to 10^7 years, ^{239}Pu will decay in excess of 300 half-lives. The release rates calculated by the model are extremely sensitive to the temperature, pH, porosity, and specific surface area assumed for dissolution of the glass. In particular measurement of specific surface area is difficult on matrices of these kind, and this variable significantly affects the final reaction rate [13].

Estimates of environmental contamination due to the dissolution of nuclear explosive melt glass produced beneath French and U.S. underground nuclear weapons test sites in the Aleutians and South Pacific are influenced by these factors:

(1) After several hundred years, relatively toxic and long-lived radionuclides (i.e., U, Pu, Am, Np, Cm) dominate the residual radionuclide source term.
(2) These radionuclides are volumetrically partitioned in nuclear explosive melt glasses.
(3) All the glasses produced are both saturated and soluble.

Predictions based on current models suggest dissolution rates are slow enough that constituent radionuclides will be released from the melt glass for more than 10^6 to 10^7 years.

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MUSSELS AND SEDIMENTS FROM THE NORTHERN ADRIATIC SEA

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Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants In most cases, their derivatives in the environment are known to be highly mutagenic and carcinogenic. PAHs are known to enter the marine environment through the spillage of petroleum, industrial discharges, atmospheric fallout and urban runoff. Bushfires can also provide a significant source of PAHs. In the water, the hydrophobic PAHs are transported with particulate organic matter (POM) and either remain suspended in the water column or are deposited in the bottom sediments. In the sediments the PAHs can be biodegraded, mineralized or transformed into highly mutagenic oxidized derivatives [1]. It is also known that PAHs may enter food chains and finally be ingested by humans through mussels, fish and crustacea. Only the mussel is confirmed as a biomonitor of PAHs in the marine environment because of its ability to accumulate, whereas fish and crustacea are capable of surviving in polluted environment based on an active oxidative enzymatic system.

In the pollution control of the marine ecosystem mussels (*Mytilus galloprovincialis*) and sediments were sampled in the Slovenian coastal sea which occupies the south-eastern part of the Gulf of Trieste which is also the northernmost part of the Adriatic Sea, Mediterranean Sea. This part of the sea is utilized for industrial, commercial (mariculture, turism) and recreational (marinas) purposes. The restricted areas like harbours, ship mooring areas and marinas are strongly affected by pollution. Therefore, five surface sediments in the central section of the Slovenian coastal sea, a sediment core in Italian part of the Gulf of Trieste and mussels samples from two bays of the Slovenian coastline (Bay of Piran and Bay of Strunjan) were collected.

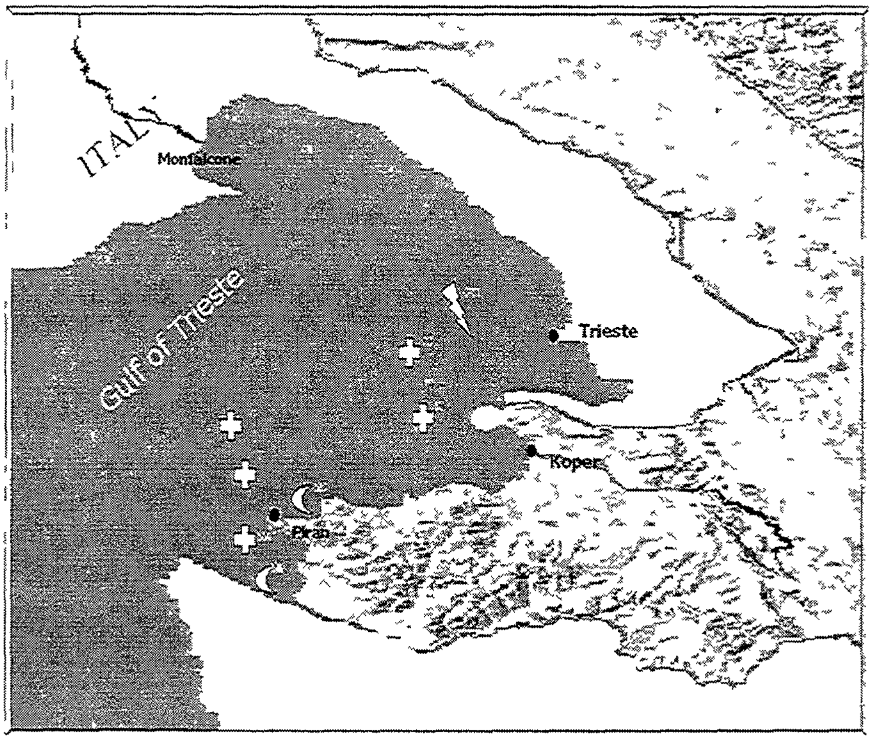

FIG 1 Locality map of the study area showing (✚) surface sediments, (☾) mussel samples and (⚡) sediment core

For determination of PAHs improved analytical procedures were applied especially in the sample preparation step. Pressurized Fluid Extraction (PFE) [2,3] as the most suitable recent extraction technique was used for the extraction of sediments and mussel tissue. Fifteen individual PAHs (naphthalene, acenaphthene, acenaphtylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene) were analyzed using GC-MS (Hewlett-Packard, 6890 Series) and quantified by using external standard test mixture of PAHs and internal standard test mixture containing four devterated PAHs.

The results in mussels sampled in the Bay of Piran and in the Bay of Strunjan are similar and show increased two- and three-ring PAHs contamination. The total amount of PAHs in mussel samples is around 600 mg kg^{-1}. When the total amount of PAHs is compared with other mussels studies [4,5] the contamination with PAHs in the Bay of Piran and in the Bay of Strunjan is similar to contamination in industrialized overseas regions.

A different situation was observed for sediment samples. Comparing the total amount of PAHs determined in surface sediments with those determined in mussels, the concentration of PAHs in surface sediments is 3-5 times lower than that determined in mussels. As expected, analysis of the sediment core sampled in the Italian part of the Gulf of Trieste shows that the highest PAHs concentration appears in the first few layers (up to 8 cm in depth), while in the following ones slight decrease of the total amount of PAHs is noted.

Observing the PAHs profiles determined in all samples (mussels, surface sediment, sediment core), the most abundant compounds are naphthalene and phenanthrene (which are most likely related to petrogenic hydrocarbons spillages) what suggest that the origin of these contaminants are shipping and maritime activity associated with the port of Koper and the port of Trieste (Italy).

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RESPONDING TO THE *SEA EMPRESS* OIL SPILL

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Abstract

The Ministry of Agriculture, Fisheries and Food (MAFF) is a government department which has responsibility in England and in Wales (acting on behalf of the Secretary of State for Wales) for controlling deposits in the sea, including approving the use of dispersants in oil spill response. MAFF also has responsibility in relation to the management of sustainable commercial fish and shellfish fisheries. Following the grounding of the tanker *Sea Empress* on 15 February 1996, over 72,000 tonnes of crude oil and bunker fuel was lost. This paper summarises the involvement of MAFF staff in the response phase, and in the subsequent assessment of the environmental impact of the oil spill and the associated clean up operations on commercial fisheries. After two and a half years of environmental monitoring and complementary research, it is concluded that the oil spill has had an insignificant impact on these fisheries beyond their closure during the incident response phase. Suggestions for further work are discussed.

1. INTRODUCTION

Following the grounding of the tanker *Sea Empress* at the entrance to Milford Haven, west Wales, on 15 February 1996, approximately 72,000 tonnes of Forties crude oil and 480 tonnes of fuel oil were spilt. This gave rise to an extensive clean-up operation, the closure of fisheries, a monitoring programme which was conducted in support of the assessments of impact and recovery, and associated research projects. The overall assessment of environmental impact was made by the Sea Empress Environmental Evaluation Committee (SEEEC), an independent body to which the results of all studies flowed, and this has been summarised both in the final report of the committee, and in the proceedings volume of a scientific conference held in Wales in 1998 [1, 2]. In this paper, we outline the role played by MAFF and CEFAS at all stages of the incident response and in the subsequent assessment of the environmental impact of the oil spill.

2. ROLE OF MAFF

The Ministry of Agriculture, Fisheries and Food (MAFF) is a government department which has responsibility in England and in Wales (acting on behalf of the Secretary of State for Wales) for controlling deposits in the sea, including the approval of the use of chemical oil dispersants applied in response to oil spills. In doing so it helps to implement the UK's international obligations under the global London Convention and the OSPAR Convention for Protecting the Marine Environment of the North East Atlantic. In order to fulfil these obligations effectively, MAFF seeks to understand and assess the potential impact of relevant activities on the marine environment through its extensive monitoring programme and through the Aquatic Environment Research and Development commission. This is divided into a series of programmes: which includes- 'Biological effects and impact assessment' and assesses the overall impact of pollutants to establish whether, individually or in combination, they are having an adverse effect on the environment. Other organisations (such as the Environment Agency, and the Department of Environment, Transport and the Regions) also have complementary environmental responsibilities.

3. ROLE OF CEFAS

CEFAS (the Centre for Environment, Fisheries and Aquaculture Science) is a government research agency and a major research contractor for MAFF. The role of CEFAS in the event of an oil or chemical incident around England and Wales is to provide advice to MAFF (and, for Wales, to the Welsh Office) regarding likely effects on commercial fish and shellfish, the conduct of the response operation, the need for fishery controls in order to protect consumers, and to design and operate any environmental monitoring programme necessary to underpin such controls.

3.1 Advice relating to the response operation

Chemical oil dispersants are only licensed for use by MAFF following testing for efficacy and toxicity [3]. Specific MAFF approval must also be obtained each time before dispersants are used in response to a particular spill. In many cases, dispersant use will not be appropriate, particularly if the spill is small or of a light oil product. However, in certain circumstances the most effective response will involve the carefully controlled aerial application of chemical dispersants [3, 5]. As fresh crude oils weather and emulsify on the sea surface, and so may no longer be amenable to dispersion after 24h at sea, then aerial dispersant spraying must be undertaken as soon as possible after release. Most of the oil spilt from the Sea Empress was lost as the tide ebbed and falling water levels allowed oil to escape from the damaged tanks, so that fresh oil was initially carried to the south where dispersant applications were made over deeper waters more than 1 km from the coast [4-6]. In all, 446 tonnes of dispersants were applied to slicks at sea, mostly between 18-22 February 1996. Consultations took place before each application began, and approval to spray was given by MAFF following advice from the MAFF District Inspector of Fisheries and CEFAS on fishery resource and contamination implications, and in liaison with nature conservation organisations such as the Countryside Council for Wales. As part of this process, "no spray" zones were agreed around the bird sanctuaries of Lundy, Skokholm and Skomer Islands and along parts of the South Wales coast so as to protect areas of shallow water, commercial shellfisheries, and environmentally sensitive areas. Following dispersant treatment, the chemically-dispersed oil mixed rapidly into the upper 10 m of the water column as fine droplets and was then transported away from the spraying site and rapidly diluted, due to the dynamic nature of the waters off south-west Wales [5]. The dispersed oil would subsequently have been biodegraded by bacteria which are naturally present in seawater, particularly in areas such as Milford Haven and the Bristol Channel which have been subject to low-level inputs of oil for many years.

3.2. Fishery closure and environmental monitoring programme

Immediately after the grounding, when oil began to be released, local fishermen implemented a voluntary fishing ban until the extent of the problem could be assessed. Once the likely spread of the oil and the area within which fish and shellfish were likely to be contaminated could be predicted with some degree of certainty, controls were implemented under the 1985 Food and Environment Protection Act (FEPA). The restriction was a precautionary measure, intended to protect consumers from potential danger from eating contaminated seafood. The limits of the zone were set on the basis of substantial observational information of the spread of oil from the *Sea Empress*, supplemented by the results of computer modelling forecasts of the movement of surface oil and dispersed oil in the water column, and the information on contamination of local fishery resources by uptake of hydrocarbons and PAH derived from the CEFAS monitoring programme. The closure area implemented under FEPA banned fishing in approximately 2000 km^2 of coastal waters [1, 2].

Monitoring of contaminant levels in fish and shellfish began as soon as the scale of the spill became clear, with the first samples being collected on 19 February. Although water and sediment samples were also analysed, the main focus of the CEFAS work was the monitoring of the uptake and loss of hydrocarbons and polycyclic aromatic hydrocarbons (PAH) by fish and shellfish. This was primarily in support of the FEPA closure order (to inform decisions on the easing of fishery restrictions), but also provided information which was used in the overall impact assessment [1]. To this end both commercial and non-commercial species were taken and analysed. The waters around south-west Wales support a diverse fishery for both fish and shellfish species, with extensive cockle and mussel beds in some intertidal areas. In the absence of comprehensive pre-spill data on levels of contamination in local seafood, the monitoring programme was designed to allow estimation of background levels by reference to areas outside the closure area (and so unaffected by the spill), and also to cover the majority of commercially exploited species. In all 880 bulked samples of fish and shellfish have been analysed from within and beyond the boundaries of the closure area, with a number of sites being sampled repetitively in order to provide "time-trend" information [2]. The locations of the fishery closure area and of the sites mentioned in the text are shown in Fig 1.

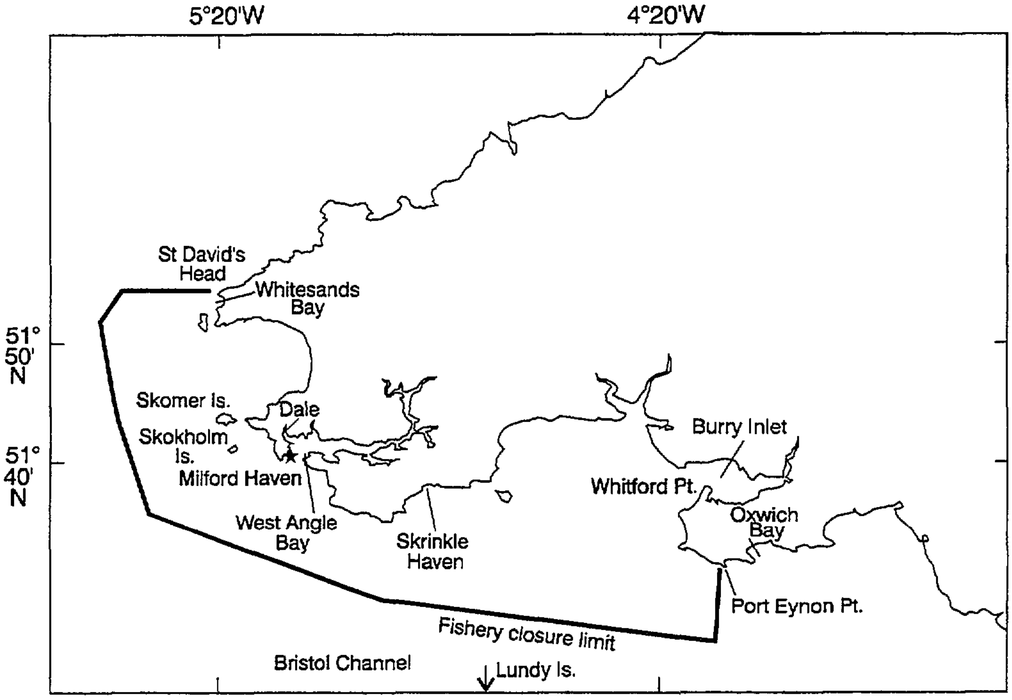

FIG. 1. The coast of south-west Wales affected by oil spilled from the Sea Empress. The line indicates the outer boundary of the fisheries closure area designated under the Food and Environment Protection Act, 1985, and the star symbol marks the grounding site at St. Ann's Head.

The criteria established for the removal of fishery restrictions were similar to those used earlier following the stranding of the *Braer* in 1993; that concentrations of hydrocarbons and PAH should be at background levels, that edible tissues should be free of taint, and that the Department of Health agreed that current levels posed no risk to consumers. The fishery restrictions were removed progressively over the 19 months following the spill. Finfish (both marine fish and salmonids) were only lightly contaminated following the spill, and controls were removed within 3 months. Restrictions on shellfish were removed over a longer time period, molluscs generally retaining contamination longer than crustaceans [2, 5]. It had been possible to lift the FEPA ban on the most important commercial and recreational fisheries within 200 days of the spill, and all fisheries were open within two years of the grounding of the *Sea Empress*. This can be compared with the *Amoco Cadiz* and *Braer* oil spills, where closures for some species and areas were still in place seven years and over five years after the incident respectively. In the case of the *Exxon Valdez*, oiling of mussels persisted for at least four years following the spill due to recontamination by oil trapped in sediments underlying mussel beds in Prince William Sound [7].

There were no obvious mortalities of adult finfish as a result of the *Sea Empress* oil spill. Large numbers of dead or moribund shellfish (mostly bivalve molluscs) were washed ashore in various locations during the weeks following the oil spill, but none of the major commercial shellfishery areas were affected [2]. Low concentrations of PAH were observed in tissues of finfish and crustacea, generally low molecular weight (2- & 3-ring) compounds absorbed directly from the water column via the gills. Much higher concentrations of a wider range of PAH (2- to 6-ring compounds) were found in bivalve molluscs, particularly those close to the grounding site within Milford Haven (e.g. at Dale and West Angle Bay; respectively more than 100,000 $\mu g\ kg^{-1}$ wet weight as the sum of the nineteen individual PAH and groups determined, and 6,800 $mg\ kg^{-1}$ as Forties crude oil, in both cases around 8 days after the initial grounding). These high concentrations resulted from direct uptake of dispersed oil droplets whilst feeding [2]. Given the locations of these animals, these were probably derived from oil dispersed naturally in the turbulent flows found around the entrance to Milford Haven. The equivalent background concentrations of summed PAH and oil in mussels from Dale in June 1997 were 75 $\mu g\ kg^{-1}$ and 19 $mg\ kg^{-1}$ respectively. Particularly high concentrations of the alkylated PAH (such as derivatives of naphthalenes, phenanthrenes and pyrenes) predominant in crude oil were attained within 1-2 weeks of the grounding, and thereafter concentrations of these components declined rapidly once the bulk oil had moved eastwards under the influence of winds and tides. PAH and oil concentrations were elevated in mussels taken throughout the closure area from Whitesands Bay, St. David's in the north, to Whitford Point in the Burry Inlet to the east, the highest concentrations of oil (up to 3,300 $mg\ kg^{-1}$) occurring at Skrinkle Haven, a small beach at which oil became entrained in sediments below the low water mark. A small elevation in tissue concentrations was also observed in mussels from Oxwich, to the east of the closure area, indicating that some oil did pass out of the closure area (probably within the water column, as it was not observed on the surface). However, the defined closure area did in practice include all the areas where PAH concentrations were of potential significance in health terms, and did not need to be extended. Statistical analysis of the PAH data for bivalve molluscs also revealed a seasonal cycle of combustion PAH concentrations apparently unrelated to the incident, with the highest concentrations being observed in the early spring and the lowest values occurring in midsummer [2]. This cycling has continued through 1998 although the maximum values vary both year by year and by location, and this process must be borne in mind when developing future monitoring programmes and assessing the potential for effects on human consumers.

4. SUPPORT FOR R&D PROJECTS

The MAFF Chief Scientist's Group (CSG) commissions research in response to policy needs, and this includes studies of the impact of pollution in the marine environment. As part of the initial environmental assessment, SEEEC recommended numerous research initiatives and a CSG representative was invited to join the SEEEC Marine Task Group in August 1996. Following discussions and agreements with other potential funders, such as the Environment Agency and the Department of the Environment, all the SEEEC requests were accommodated. For MAFF, six projects were commissioned, and these were in many cases extended or revised in the light of the initial findings so as to maximise the information obtained. The commissioned research included enhancement of the oil spill modelling capability, as well as fishery stock assessment studies and investigations of sub-cellular impacts on fish and molluscs [2]. Results from the research programme helped assess the short-term impact of the oil spill on commercial fish stocks and their recovery over a two year period.

The juveniles of the commercially important fish species the sea bass (*Dicentrarchus labrax*) spend much of their early life in very shallow water. During 1996, sampling of bass indicated the late arrival of adult fish relative to earlier years, delayed spawning times, and a reduced abundance of 0-group (young of the year) bass in oil-affected areas compared with unaffected areas nearby. Concern was expressed that this may be a result of exposure to Sea Empress oil, and sampling continued in 1997 to assess spawning dates, arrival times, distribution, condition and growth rates of 0-group and 1-group (i.e. fish spawned in 1996 and 1997). It was concluded that the anomalies observed were more likely to have been due to natural phenomena, with a small possibility that the oil spillage and associated clean-up operations had had some impact on bass eggs and larval stages [8, 9]. For herring (*Clupea harengus*) the stock is of minor commercial importance, but the adults migrate in February and the eggs of this fish are deposited close to the site of the oil spill, and so these fish were considered to be a good environmental indicator. Studies undertaken in 1997 and 1998 to assess the stock concluded that there was no demonstrable effect from the oil spill. [10, 11]. A study of the new whelk (*Buccinum undatum*) fishery off South Wales had provided extensive catch per unit effort (CPUE) data for these molluscs. The limited data available on resumption of the fishery did not show that there was a significant reduction in CPUE, and by inference therefore no significant reduction in the population density of the whelks [10].

To complement research undertaken by the Environment Agency, the possible effects of the spilled oil or of the use of oil dispersants on the olfactory system of salmonids (*Salmo salar* L.) was studied. The olfactory system is used during the spawning migration to identify the fishes' home rivers, and electrophysiological tests conducted in the laboratory on young fish exposed to *Sea Empress* oil had shown that a pheromone and an amino acid were significantly reduced or abolished, suggesting potential homing difficulties for wild fish [12].

Research funded jointly by MAFF and the Department of the Environment (latterly the Department of the Environment, Transport and the Regions) on the occurrence of DNA-adducts had demonstrated that some genetic damage had occurred in fish and mussels during 1996, but a significant recovery was seen in 1997 [2, 13, 14]. It was therefore not clear that the exposure to *Sea Empress* oil would result in the eventual generation of tumours in commercial species of fish, as the damage may have been repaired in the interim period. Further sampling of biota will be undertaken in 1998 and 1999 for analysis of PAH in tissues, in order to assess any longer term impact of the oil spill.

5. CONCLUSIONS

Interpreting environmental impacts is often difficult because of the natural variability inherent in biological systems. To overcome this problem would require extensive (and expensive) long-term monitoring of key species. From the environmental monitoring programme and complementary research undertaken on behalf of MAFF, we conclude that the *Sea Empress* oil spill did not significantly impact commercial fisheries beyond their closure during the incident response phase. The environmental effects of the *Sea Empress* oil spill were less severe than could have been expected on the basis of the quantity of oil spilt and in comparison with other spills of a similar magnitude. This was at least partly due to the timing of the spill in February 1996, as the activity level of many species is low at this time of year and feeding is reduced. Many lessons have been learnt and will be taken forward in readiness for future incidents. Within MAFF, as part of the continuous improvement in our emergency response capability, improvements in information technology gathering and transfer should mean that computer models which are used to forecast the movements of spilled oil and chemicals may in future include biological, chemical and physical parameters so as to also assist in prediction of the impact of spillages. Generally the modelling should be targeted on key areas, such as ports with oil refineries and terminals, busy waterways such as the Dover Strait, and restricted navigational areas off rocky shores where incidents are more likely to occur. The SEEEC committee has suggested in its report that an Impact Assessment Group (IAG) should be established when responding to future major spills, to carry out the necessary monitoring and environmental measurements. The IAG would need to focus on both the short-term needs and longer-term assessments and to co-operate with the public health authorities, as well as to co-ordinate inputs from interested bodies including MAFF, the Environment Agency, and conservation bodies. The SEEEC committee report also indicates that there have been very few major long-term environmental effects as a result of the spill [1, 2]. Additional environmental monitoring will be required in order to derive adequate background data for use in future incidents, and work was undertaken in 1996/97 by MAFF and CEFAS to determine PAH concentrations in shellfish from commercial beds around England and Wales (as yet unpublished data). A review of the availability of baseline environmental data and the adoption and validation of standard sampling and analytical methods would also be undertaken in preparation for future incident response, and these arrangements are expected to be formalised within the revised UK National Contingency Plan. This is currently being updated by the Marine Pollution Control Unit in the light of lessons learned during the *Sea Empress* incident.

Acknowledgement

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ASSESSMENT OF PHENOLS AND OIL POLLUTION IN THE EASTERN LEVANTINE (WINTER 1992)

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Abstract

Phenols and dissolved/dispersed petroleum hydrocarbons were determined to assess the level of organic pollution in the waters of the eastern Levantine sea (eastern Mediterranean) and Syrian shoreline. Sampling program was carried out in February 1992. The phenols concentrations were ranged between non detectable values and 0.88 µg/l. The dissolved/dispersed petroleum hydrocarbons concentrations were averaged from 1 to 37.5 µg/l in the studied seawater, 65.8% of petroleum hydrocarbons samples were ranged between 1 and 10 µg/l. The distribution of phenols and dissolved/dispersed petroleum hydrocarbons in seawater indicate to be governed by water circulation and external sources.

1. INTRODUCTION

As a semi-enclosed sea, the Mediterranean is usually represented as depository for anthropogenic wastes, and is subjected to man's greatest impact, particularly in highly industrialized coastal areas [1, 2]. Most of the pollution accumulates there, bringing about dramatical transformations in ecosystems, as evidenced by a variety of a variable data on ecological conditions [3]. Also, the water currents play an important role on horizontal and vertical distribution of different pollutants, regarding to their degree of stability in seawater. Several studies were done concerning oil pollution in the Mediterranean sea [4, 5, 6, 7] ; however, a few ones were realized in the marine sector situated between the island of Cyprus and the Syrian coast [8, 9]. In the same way, a very limited number of studies was done on the distribution of phenolic compounds in some coastal areas of the eastern Mediterranean seawater [10, 11].

The aim of this study is to assess the level of phenols and dissolved/dispersed petroleum hydrocarbons in the water of the eastern part of Mediterranean sea, situated between the island of Cyprus and the Syrian coast.

2. MATERIALS AND METHODS

Thirty eight sampling stations were chosen in the marine sector located between the island of Cyprus and the Syrian coast (Figure 1). Water samples were collected from 15 to 22 February 1992, during the 24Th cruise of Russian Oceanographic R/V "Vityaz"; they were taken from 0.5 meter below water surface, using 2.5 liters pre-cleaned Labe-Line water sampler. Phenols concentrations were determined using 4, aminoantipyrine spectrophotometric method with distillation procedure [12]; the precision is 5% for a phenols concentration of 1 µg/l. For dissolved and dispersed petroleum hydrocarbons analysis, seawater samples were extracted twice with free hydrocarbons n-hexane [13]. Dissolved/dispersed petroleum hydrocarbons concentrations were evaluated by Spectrophotmetric

technique [8]; the absorbances were standardized later by spectrofluorimetric technique using chrysene as an intercomparison chemical standard [13]; the
precision is 5% for a petroleum hydrocarbons concentration of 10 µg/l.

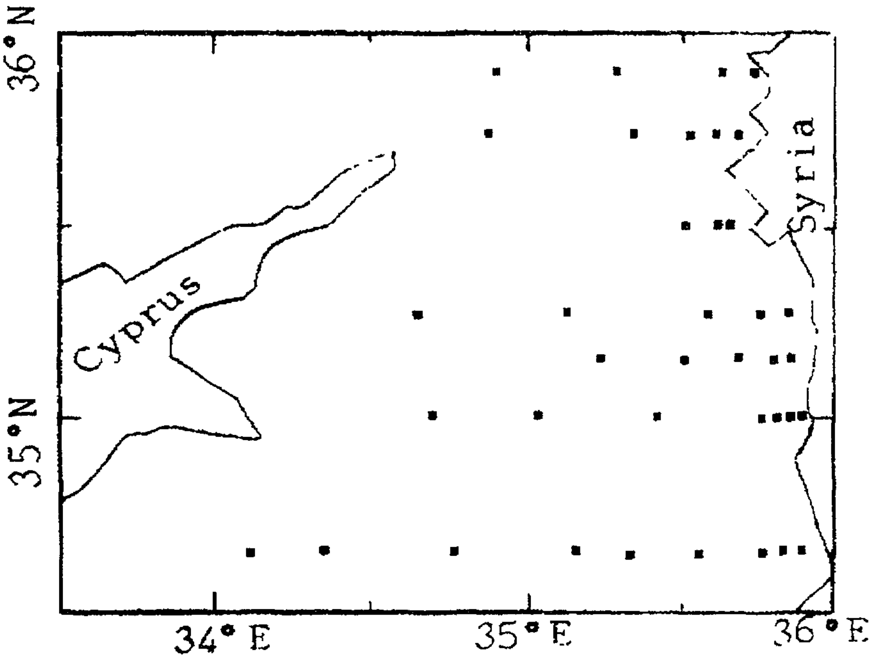

FIG. 1. Geographic localization of oceanographic stations

3. RESULTS AND DISCUSSION

Phenols concentrations were ranged between non detectable values and 0.88 µg/l, showed irregular horizontal distribution. A relatively high concentrations (>0.5 µg/l) were observed in the southern transection off Syrian coast, and in the middle part of Syrian coast; this distribution is in accordance with that recorded for the phenols distribution in surface Syrian coastal waters [8]. Two principal factors influenced this distribution: water currents and land based sources. The vertical distribution of phenols showed a maximal concentration in superficial waters, then decreased with depth until the thermocline level, under this level, phenols concentration is almost constant at very lower values, and is under limit of detection in Levantine deep waters (>500 m.).

Dissolved and dispersed petroleum hydrocarbons concentrations were ranged between 1 and 37.5 µg/l; 65.8% of samples are ranged between 1-10, 28.9% between 10-20 and only two values (located in the southern transection) between 20-37.5 µg/l. Relatively high values (>10 µg/l) were observed in the southern transection of the studied area and in the middle part of Syrian coast, reflecting the impact of external petroleum hydrocarbons sources on their distribution in seawaters, especially near petroleum terminals and in the area of shipping activities. In open sea, many ships and tankers probably still practice daballasting release of wash waters and bilge. Moreover, this distribution is also influenced by general circulation of seawaters. Concerning the level of dissolved/dispersed petroleum hydrocarbons, our results are in accordance with those obtained for the Syrian Coastal waters [9] and for the Eastern Mediterranean sea [14].

The highest concentrations of phenols and dissolved/dispersed petroleum hydrocarbons were registered facing the middle part of the Syrian coast and mostly in the southern transection (34°40'N). These maximal levels can be related directly to the anthropogenic factors and water currents; the mean current in the investigated area, directed from south and south-west to north [15, 16], can enrich the southern part with these organic pollutants.

TABLE I. MEAN AND RANGE VALUES (IN PARENTHESES) OF PHENOLS CONCENTRATIONS (µG/L) IN SURFACE SEAWATER OF DIFFERENT STUDIED TRANSECTIONS.

Latitude	Mean (Range) concentrations (µg/l)	n	σ_{n-1}
34° 40′ N	0.40 (0.11-0.84)	9	0.239
35° 00′ N	0.20 (0.02-0.35)	7	0.106
35° 10′ N	0.03 (0.02-0.05)	5	0.014
35° 20′ N	0.20 (nd -0.28)	5	0.113
35° 30′ N	0.18 (0.11-0.28)	3	0.091
35° 40′ N	0.45 (0.02-0.88)	5	0.413
35° 50′ N	0.04 (0.01-0.07)	4	0.035

TABLE II. MEAN AND RANGE VALUES (IN PARENTHESES) OF DISSOLVED AND DISPERSED PETROLEUM HYDROCARBONS CONCENTRATIONS (µG/L) IN SURFACE SEAWATER OF DIFFERENT STUDIED TRANSECTIONS.

Latitude	Mean (Range) concentrations (µg/l)	n	σ_{n-1}
34° 40′ N	18.89 (10.4-37.5)	9	8.656
35° 00′ N	7.79 (4.1-13.4)	7	3.789
35° 10′ N	5.98 (4.1-10.3)	5	2.579
35° 20′ N	3.72 (2.2- 5.1)	5	1.105
35° 30′ N	1.77 (1.1- 3.1)	3	1.155
35° 40′ N	2.32 (1.1- 4.1)	5	1.301
35° 50′ N	1.65 (1.1- 2.2)	4	0.635

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MODELLING THE TRANSPORT OF SEDIMENTS AND PLUTONIUM FROM THE MURUROA LAGOON

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Abstract

The paper deals with the three-dimensional simulation of resuspension and transport of sediments from the Mururoa lagoon into the Pacific Ocean. These sediments were contaminated mainly by plutonium during French nuclear tests (from 1966 to 1996). Two cases were simulated: 'Normal conditions', taking into account permanent action of trade winds and tides and 'storm conditions', where the effect of a tropical cyclone with maximum wind velocity of 150 km/h and with a frequency of 1 storm per 10 years is simulated. The final results show, that the normal conditions cause an annual outflow of 8 x 10^4 tons of sediment and 8 GBq of plutonium, while one tropical cyclone would cause outflow of 3.9 x 10^6 tons of sediment and about 0.7 TBq of plutonium.

1. INTRODUCTION

Between 1966 and 1996, France conducted 46 atmospheric and 147 underground experiments at the Mururoa and Fangataufa Atolls in French Polynesia. Recent measurements in both lagoons have shown that the sediment is contaminated primarily by isotopes of plutonium, which for the most part is the consequence of the atmospheric tests. As part of the study *The Radiological Situation at the Atolls of Mururoa and Fangataufa* under the International Atomic Energy Agency, modelling of the transport of the contaminated bottom sediment of the Mururoa lagoon was undertaken to asses its radiological impact.

The Mururoa atoll is situated in the Tuamotu Archipelago. Its maximum dimensions are approx. 25 x 10 km (see Fig. 1). The maximum depth of the lagoon is 55 m, its average depth being 33 m. The exchange of water with the Pacific Ocean is enabled mainly through the pass in the NW rim, which is 8 km long with average depth of 8 m. The main objective of this part of the study is to provide answers to the following questions:

(a) What amount of bottom sediments in the Mururoa lagoon would be resuspended and transported out of the lagoon into the Pacific Ocean per year according to different scenarios (circulation due to trade wind and tide, tropical cyclones)?

(b) What is the outflow of radionuclides transported with the sediments out of the lagoon per year and by each typical cyclone.

The need for using modelling tools is obvious. It is practically impossible to carry out extensive measurements, which could provide us with the necessary answers, especially in the case of storm conditions. However, measurements necessary for calibration and verification of the model results.

2. METHODOLOGY

A three-dimensional (3D) model PCFLOW3D, developed at the Ljubljana University, was used for the simulation of water circulation in the lagoon and for the sediment resuspension and transport inside the lagoon and out of it (Rajar and Cetina [1]). The integrated model is composed of several modules. Only hydrodynamic and sediment transport modules were used in this study.

The hydrodynamic module, which simulates water circulation in the lagoon in different conditions is three-dimensional (3D) and non-linear. A one-equation turbulence model of Koutitas is included for the calculation of vertical turbulent viscosity. The finite-volume numerical method is used for the solution of the basic equations. The module is baroclinic, but for the Mururoa case the simulations were carried out with uniform water density.

Sediment transport module is based on the equations of Van Rijn [2]. Resuspension of sediment from the bottom depends on the bottom shear stress, caused by current velocities and waves. The transport and dispersion of sediments inside the lagoon and out of it (through the pass) was simulated depending on the combined action of currents and waves.

It was estimated that a significant amount of sediment can also be washed out of the lagoon over the SE and S rim during cyclones. To determine the water discharge over the rim, all the available data on the observations of the phenomena (wind, waves, storm surge) in the Mururoa and similar lagoons were taken into account [3] together with an empirical procedure for the calculation of water discharge due to wave overtopping of the rim described in Sylvester [4].

The discharge of sediment bound radionuclides from the lagoon for different scenarios was calculated with the following assumptions:

(a) Only $^{239+240}$Pu was taken into account, as the most important element bound to sediment.

(b) The decay rate was neglected.

(c) With the concentration of radionuclides in sediment Csed (Bq/kg) given as input data, the outflow discharge of the sediment bound radionuclides R (Bq/year) was calculated to be **R (Bq/year) = Csed (Bq/kg) * Qsed (kg/year),** where Qsed is the outflow discharge of sediment.

Data on bottom sediments were taken from the report of Masse and Mussa, [5], based on measurements. The D50 particle diameter is 0.1 mm.

3. SIMULATED CASES AND RESULTS

3.1 Normal conditions: Effect of trade winds and tides

Normal' conditions, governing the circulation during the greater part of the year were taken into account first: trade wind, easterly of 8 m/s, together with the influence of tides, with an amplitude of 0.3 m and a period of 12.4 h.

Hydrodynamic simulation of current velocities was carried out first (Fig. 1). The resulting velocity fields are very near to the results of Tartinville et al. [6]. The wave height caused by east wind of 8 m/s increases from east to west in the lagoon and attains a maximum value of nearly 1 meter near the westernmost coast.

Near the pass, the velocities are of the order of 20 cm/s. Most of the sediment resuspension occurs in the vicinity of the pass, and some in the shallow water along the southern coast. There is a resuspension and transport of suspended sediments out of the lagoon during ebb tide. The simulation results show that during one tidal cycle a mass of 1.1 * 10^5 kg is washed out of the lagoon. This results in a rate of sediment outflow due to wind and tide of about 80 000 tons/year, which corresponds to about 3 kg/s over the whole cross section of the pass).

The outwashed mass of 80 000 tons would mean an erosion of 0.4 mm/year over the whole lagoon. This value is given only for illustrative purposes, because the erosion would not be distributed uniformly over the lagoon, and some sediments are also formed and deposited by various processes. No measurements of this phenomenon were available for the Mururoa lagoon.

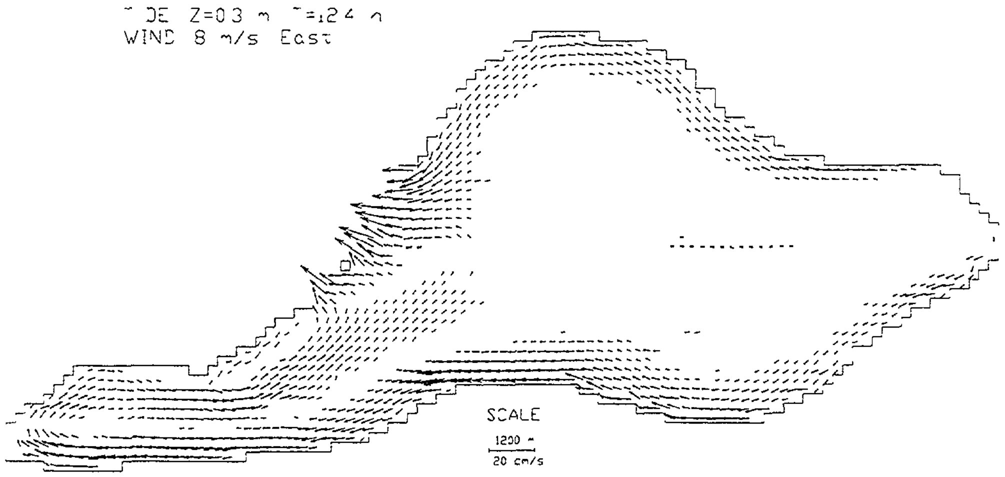

FIG. 1. Depth-averaged velocities at ebb tide: Normal conditions.

3.2 Storm Conditions

There is evidence of tropical cyclones in the region of Mururoa and also of their impact on the sediment transport. The forcing conditions for this case were determined mainly from [3]. The "*maximum historically probable cyclone*" in this region has been defined as a NW wind of 80 knots (150 km/h or 42 m/s). Fig. 2 shows the assumed time development of wind speed for such a storm. The duration of maximum wind speed was estimated to be 4 hours. The NW direction of the wind was assumed, although during the passage of the cyclone it is changing.

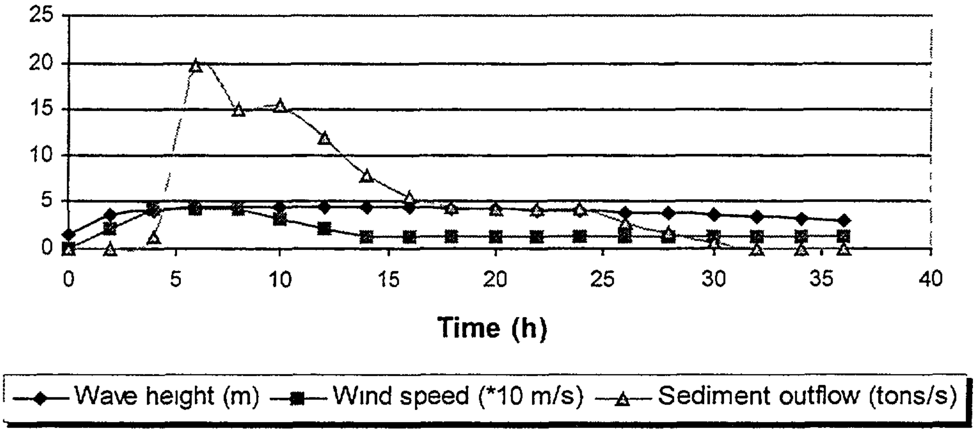

FIG. 2. Wave height, wind speed and sediment outflow through the pass : Storm conditions.

The frequency of such cyclones was estimated from [3] to be about 0.1 per year (one cyclone per 10 years). Although the statistical data show smaller frequency during the last 100 years, there were 5 cyclones in the first half of 1983 in the Tuamotu Archipelago (though not all of them touched Mururoa). Gabrie and Salvat [7] describe the frequency in the region of Mururoa to be "four to eight per century".

Resulting flow of water and sediments through the pass. The 3D hydrodynamic simulations have shown surface velocities of the order of 1.3 m/s and maximum depth-averaged velocities (Fig. 3) to the order of 40-50 cm/s, which, for the most part, is in agreement with the values from [3]. Wave height is described to be almost 10 m in the ocean and about 5 m in the central part of the lagoon (due to transmission through the pass, and due to wave diffraction, refraction and reflection). This was taken into account in the hydrodynamic and sediment transport simulations.

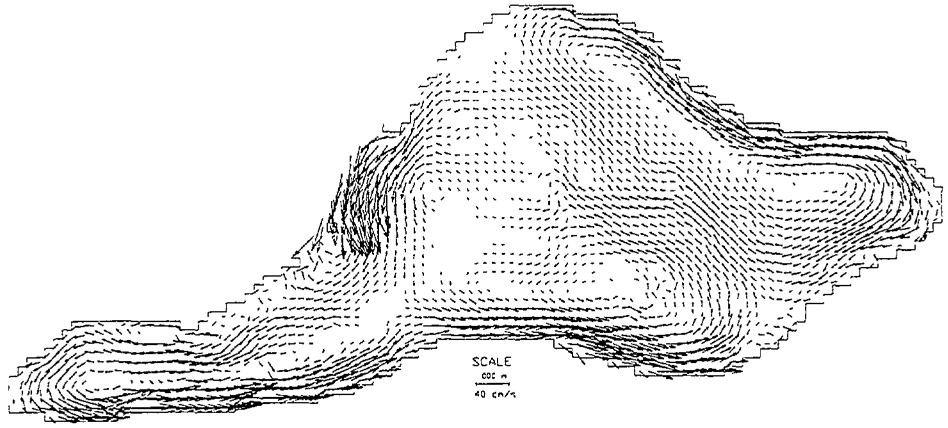

FIG. 3. Depth-averaged velocities for Storm conditions (wind NW, 150 km/h)

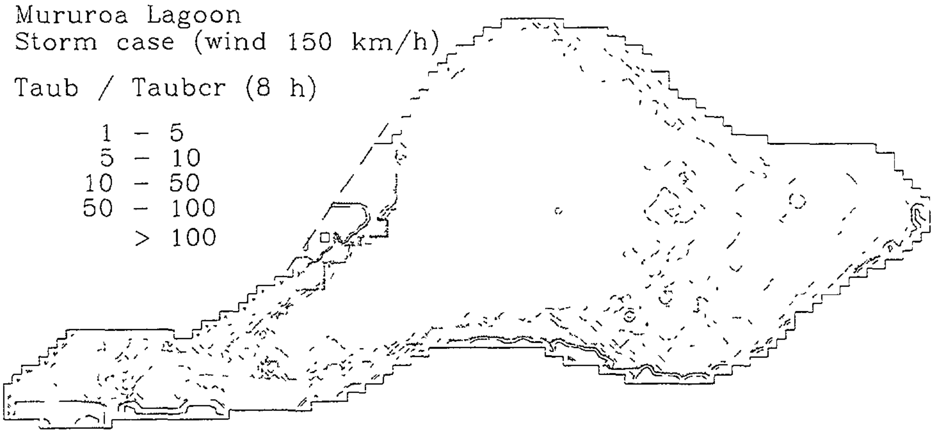

FIG. 4. Ratio of bottom shear stress to critical shear stress: Storm conditions.

Fig. 4 shows the distribution of the ration of the bottom shear stress to the critical shear stress. Wherever this ratio is greater than 1.0 resuspension of the sediment will occur. The final results of the modelling are shown in Fig. 2. The time integration of the sediment discharge over the storm duration shows that about 720 000 tons of sediment are transported out of the lagoon during one storm event.

Flow of water and sediment over the SE rim of the atoll. For wind of 150 km/h in the lagoon, from the NW, the height of the waves along the SE and S rim of the atoll, was estimated to be 5 metres (Ref. [3]). The height of the rim above the mean water level is between 1 and 3 metres. It is expected that a cyclone would cause overtopping of the rim, with significant discharge of both water and sediment over the rim into the ocean. This is confirmed by observations from similar atolls. Lachenaud [3] describes observations on several atolls during cyclones, mostly with the "greatest part of the atoll submerged". A combination of data from the aforementioned paper and an empirical procedure from Sylvester [4] was used to determine the water discharge and another procedure from [2] was used to determine the sediment concentration and further on the sediment outflow.

Basic data and assumptions for the calculations are given in Fig. 5. The height of the rim above the mean water level is taken to be 1.5 m. As the wind shear stress would cause storm surge of about 0.5 m at the SE side of the lagoon, we have taken into account the average height of the rim over the storm water level (SWL in Fig. 5) to be only 1 meter. According to [4], it was calculated that the wave run-up over the mean water level is Ro = 3.5 m. Due to the fact, that the atoll is about 300 to 400 m wide, we estimated the effective wave run-up to be diminished to 2.7 m. (Together with a 0.5 m rise of the water level due to storm surge the total rise of the water level over the mean is 3.2 m which is in agreement with observations from [3]). According to Sylvester [4], with the aforementioned values of parameters we obtain a discharge of water of 0.5 m3/s/m. Over the length of 20 km and over 6 hours of the storm duration, a volume of 2.16 * 10^8 m3 of water would flow over the rim.

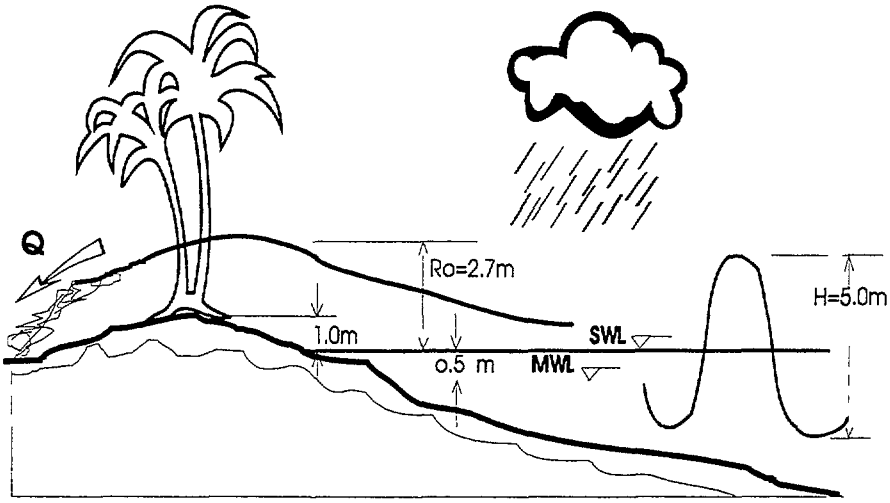

FIG. 5. Parameters for computation of overflow over the atoll rim: Storm conditions. MWL: mean water level, SWL: storm water level, Ro: wave run-up, Q:water discharge over rim.

For the conditions described, the sediment concentration near the bottom of the lagoon would be about 50 kg/m3. As high mixing over the depth is to be expected, we have assumed that the depth-averaged concentration will be 0.6 of this, i.e. 30 kg/m3. This results in a mass of 6.5 * 10^6 tons of sediments washed out of the lagoon over the 20 km of the rim during one storm event. However, this outflow of sediment could only be realistic if the whole area of the shallow sea near the SE to S rim, the beach and the nearby part of the atoll were all completely erodible. As there are parts of the described region which are not, or are only partly erodible (corral reefs, carbonate, structures...) we estimated that only 50 % of the calculated sediment mass would be washed out. Hence the total mass of sediments, washed over the rim during one storm event would be **3.3 * 10^6 tons.** This is roughly 4.5 times the mass, which would be washed out of the lagoon *through the pass* during the same storm event.

A simple calculation shows that this would cause a beach erosion about 0.5 m deep, which is calculated over the whole 20 km length of the rim and over 300 m width (this would be partly in the shallow sea near the beach, along the beach itself and partly on the atoll). In fact the erosion would be concentrated along some weaker, more erodible sections. Cases of total erosion of some parts of atolls by cyclones confirm that such erosion is realistic (The Caye Caulkner Atoll in Belize was recently cut in two by a cyclone and a channel was formed in between).

In total, the amount of sediment washed out of the lagoon during one storm is roughly **4 x 10^6 tons.** This is equivalent to a removal (erosion) of a layer about 2 cm thick *over the entire lagoon bottom.* In reality this erosion would be distributed very non-uniformly.

4. OUTFLOW OF RADIONUCLIDES

The average $^{239+240}$Pu concentration in the top 10 cm of the bottom sediment in the Mururoa lagoon has been estimated, on the basis of French data and results obtained from the Study, to be 500 Bq/kg. For the regions near the pass and in the vicinity of the SE rim, the concentration is estimated to be much lower, about 20 Bq/kg. As during both cases (normal and storm conditions) the sediment is partly, but not entirely, mixed over the lagoon, we estimated the concentration near the pass and in the vicinity of the SE rim to be about 100 Bq/kg.

The final result is: The amount of radioactive material washed out through the pass by permanent action of the trade winds and tides would be about **8 GBq/year**, and the total outflow of plutonium during one storm event (through the pass and over the rim) is **0.7 TBq/storm.**

The estimated outflow of sediment and plutonium from the Mururoa lagoon to the open ocean is summarised in Table I. The dominant release of plutonium will occur during storm conditions. Due to some not precisely known data (thickness of sediment cover on the bottom, topography of the atoll rim) and to some rough estimations in the calculations (empirical formulae for calculation of the overtopping of the rim due to storm surge and waves) the estimates of the outflow of sediments and plutonium are considered to be accurate to within a factor of three.

TABLE I: SEDIMENT AND PLUTONIUM OUTFLOW FROM MURUROA LAGOON

	Wind-tide case		**Storm case**	
	Sediment (t/year)	**$^{239+240}$Pu (Bq/y)**	**Sediment (t/storm)**	**$^{239+240}$Pu (Bq/storm)**
Through pass	*8 x 10^4*	*8 x 10^9*	*7.2 x 10^5*	*3.6 x 10^{11}*
Over SE rim			*3.2 x 10^6*	*3.3 x 10^{11}*
TOTAL	**8 x 10^4**	**8 x 10^9**	**3.9 x 10^6**	**6.9 x 10^{11}**

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LONG RANGE TRANSPORT OF ^{129}I AND ^{137}Cs IN THE NORDIC SEAS AND THE ARTIC OCEAN

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Abstract

Transport of ^{129}I and ^{137}Cs from the Sellafield and La Hague reprocessing plants to the Nordic seas and the Artic ocean has been investigated.

1. INTRODUCTION

Since several decades radionuclides, including ^{129}I and ^{137}Cs, have been released from the European reprocessing plants in Sellafield (UK) and La Hague (France). For several reasons both radionuclides are of great relevance for the oceanography of the Northern Seas and the Arctic Ocean:

- They are ideal tracers for the fate of water soluble contaminants originating from the highly idustrialized zones in western Europe to the high latitude oceans. For both tracers in the Arctic Ocean the European reprocessing plants are the major sources.
- Both release functions are well documented at the two point sources.
- Moreover, due to differences in the release functions and an almost conservative behaviour in the water column, the ^{129}I/^{137}Cs tracer pair can be used to deduce tracer transit times from a reference point in the Norwegian Coastal Current since the year 1987.

2. LONG-RANGE TRANSPORT

To investigate the long-range transport of the two tracers, a coupled ice-ocean general circulation model of the Arctic, the Nordic Seas and the northern North Atlantic is used [1]. It is run for three decades and driven with monthly mean climatological atmospheric forcing. The resulting seasonal cycle of the circulation in turn is used to force the advection and dispersion of the tracers. A comparison of the simulated tracer transit times with the measured and ^{137}Cs values serves as a validation for the model run. On the other hand, the model results can help interpreting the measured radionuclide concentrations in the deep interior Arctic Ocean.

In the model, a proxy time series for ^{129}I and concentrations at the reference point is used as a tracer source [2] (Fig. 1). It includes the contributions from the two reprocessing plants and the additional source in the Norwegian Coastal Current resulting from the Chernobyl accident.The model is run for the period 1965-1995.

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The simulated large scale patterns of ^{129}I and ^{137}Cs concentrations show a poleward advection with the Norwegian Coastal Current and an inflow into the Barents Sea. Part of the tracers continue northeastward along the west coast of Nowaya Semlya, while the other part enters the Kara Sea. Here a large inflow of riverwater from the rivers Ob and Yenessei takes place.

The contaminant dispersion continues at the surface, in the halocline and in the Atlantic Water layer of the Arctic Ocean. Fig. 2 depicts a horizontal cut through the model area in a depth of 400 m, the central Atlantic Water layer for the year 1995. Entering from the St.Anna Trough of the northern Kara Sea, the contaminated water masses move along the continental slope eastward and bifurcate at the Lomonossov Ridge. The major part enters the Canadian Basin following the slope further on and a smaller part turns northward along the Ridge. A second bifurcation happens at the Chuckchi Plateau, where the outer part of the flow circulates anticyclonically around the plateau. A horizontal section made from USS Cavalla in 1995 [3] in the upper Atlantic Water layer shows minimum concentration along the southern slope of the Alpha Ridge (Fig. 3). The same feature is seen in the model and can be clearly identified as a branch of relatively old (i.e. low iodine) water turning eastward from the Canadian Slope. The model runs suggest this water to be older than 30 years.

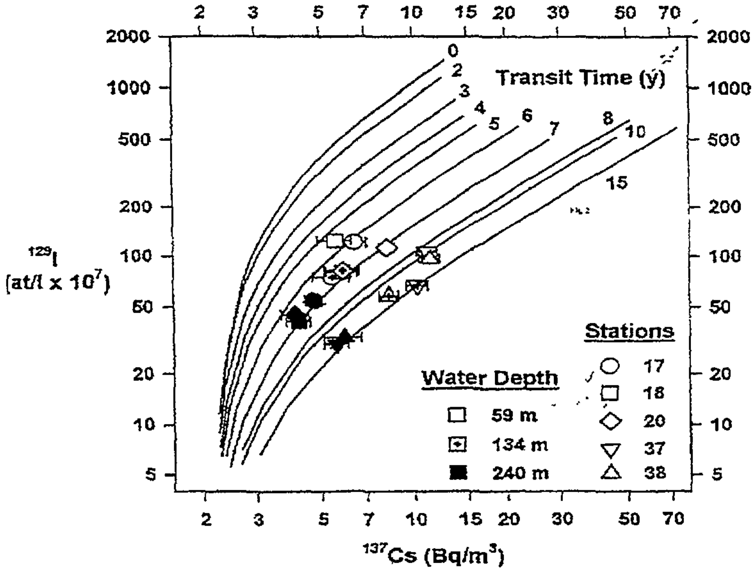


FIG.1: Proxy time series of ^{129}I and ^{137}Cs concentrations and their ratio in the Norwegian Coastal Current as estimated according to [2].

Fig. 4a shows the concentration of the modelled ^{129}I along the track of the *Arctic Ocean Section 1994* . The simulated and measured values [4] are in good agreement. This holds for the strong front between Atlantic and Pacific originated water above the Mendeleev Ridge, and for the deep maximum on the Chuckchi Slope.

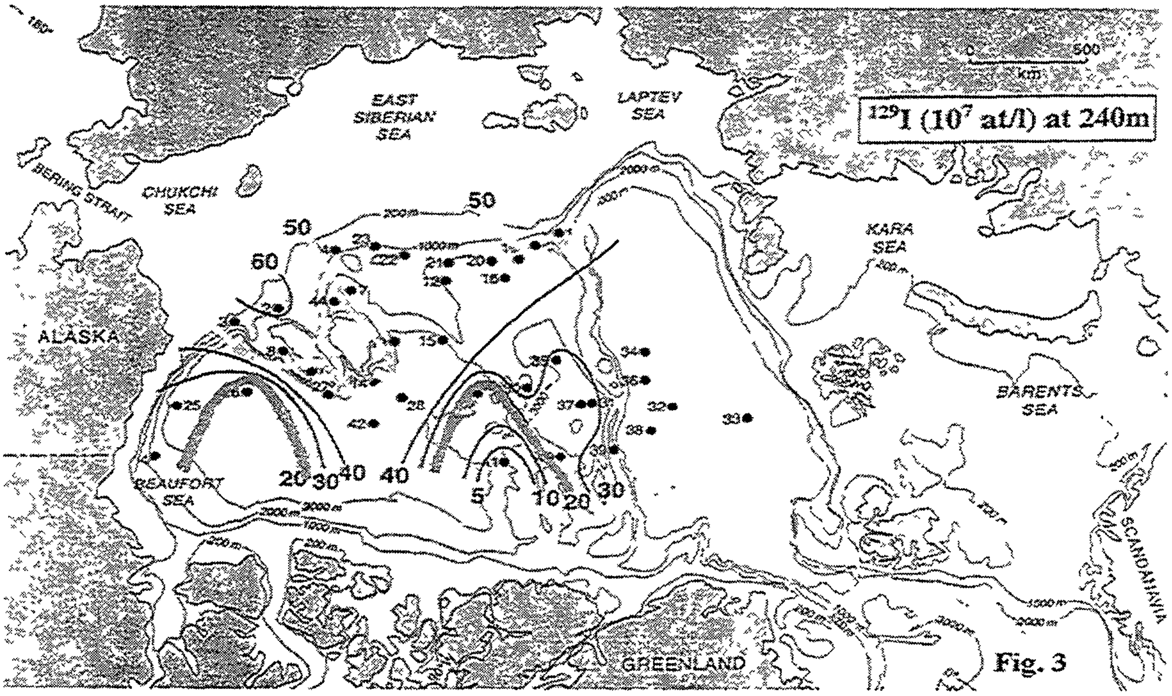


FIG.2: Concentrations of ^{129}I in 240 m depth as measured in 1995 from the submarine USS Cavalla [from 3].

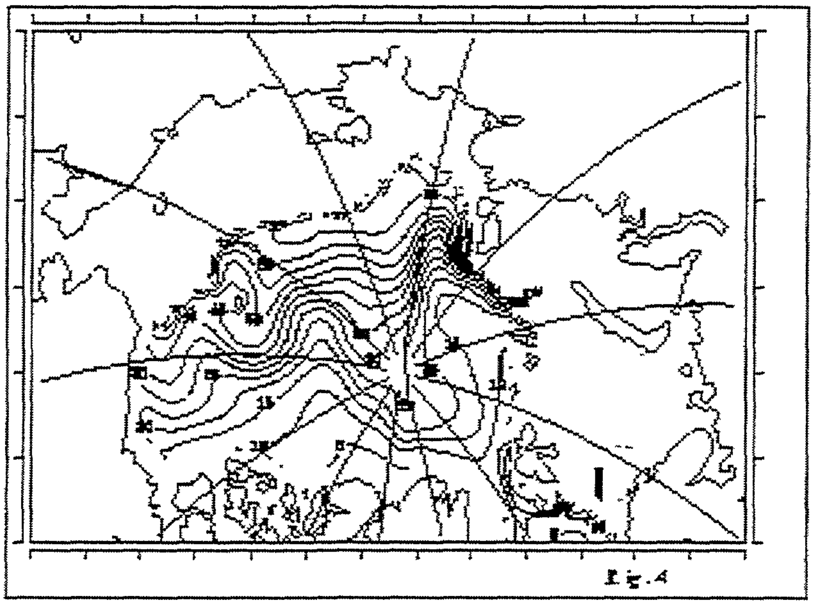
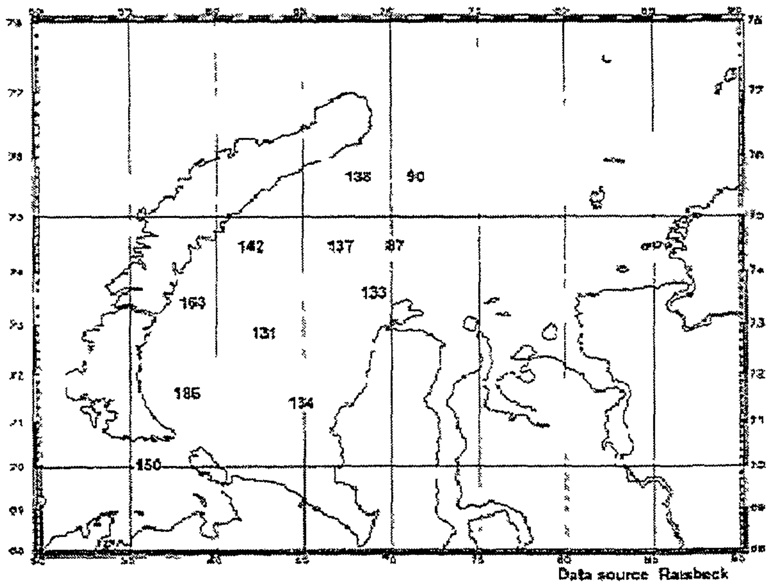


FIG.3: Concentrations of ^{129}I in units of 10^{7} atoms/litre in 400 m depth as modelled for the year 1995.

1992

^{129}I [10^7 atoms/l] in Sea Water of the Kara Sea



1995

^{129}I [10^7 atoms/l] in Sea Water of the Kara Sea

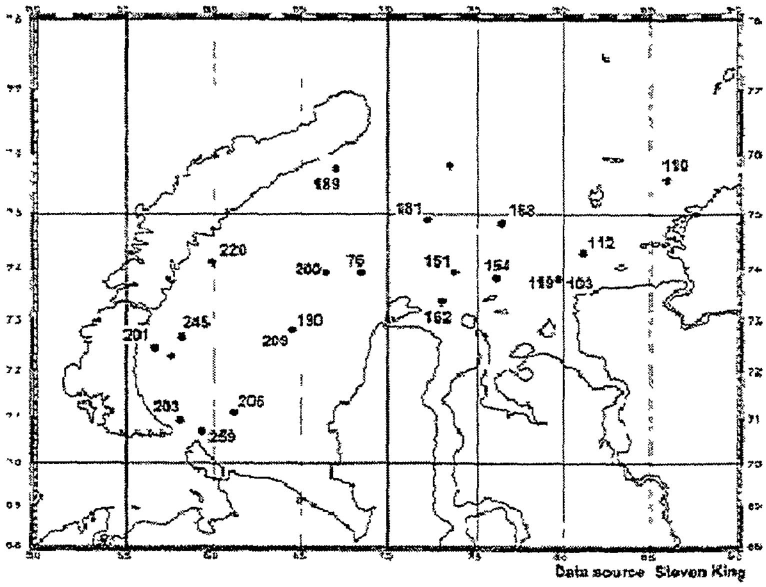


Fig. 5a

FIG.4a: Concentrations of ^{129}I in units of 10 ^{7} atoms/litre at the surface of the Kara Sea observed in 1992 [5] and 1995 [King, pers.comm.].

The study with the circulation model reveals the entirely different advection pathways and transit times in the different layers of the Arctic Ocean. The transit times can now be compared to transit times which have been calculated using the tracer pair ^{129}I and ^{137}Cs and a simple mixing approach [3] The circulation model and the data point to surface transit times from the reference point in the NCC to the Kara Sea of 2-4 years and 5-7 years to the eastern European Basin. In the lower halocline and upper Atlantic Water 5-8 years are needed to reach the eastern Siberian Slope. For the longer transit times in the Atlantic Water the model gives 15-20 years to the Fram Strait along the Lomonossov Ridge and to the Chuckchi Plateau. The data are not yet appropriate for transit times longer than 10 years.

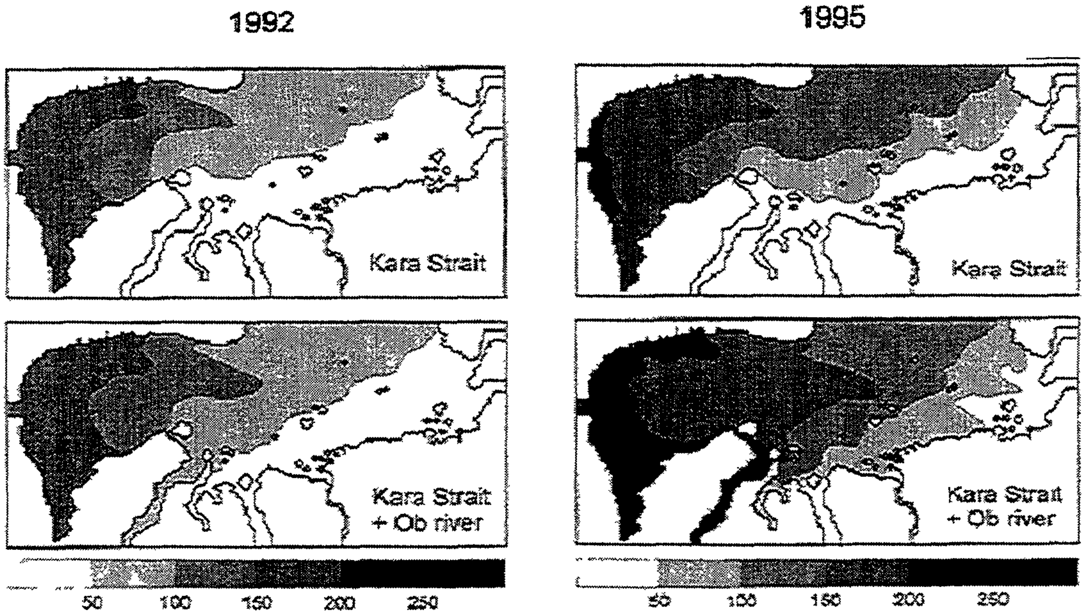


Fig. 5b

FIG .4b. Concentrations of ^{129}I *in units of* 10^{7} *atoms/litre at the surface of the Kara Sea as modeled for the years 1992 and 1995. For each year two experiments with and without input from the Ob river in addition to the Kara Strait input is shown.*

However, the model results disagree with high values of ^{129}I in the coastal Kara Sea, measured in the mid 1990s [5, Steven King, pers. comm.]. In order to investigate this disagreement, an additional high resolution Kara Sea model [6] is used to simulate the fine scale structure for ^{129}I and ^{137}Cs distributions as a result of inflowing NCC and Atlantic Waters and the mixing with, potentially contaminated, river sources. ^{129}I inflow values from the large-scale circulation model are used at the Kara Strait. Experiments with an additional source of variable strength in the Ob river are performed. It turns out that only the addition of a source of ^{129}I in the Ob river with a concentration of 150 x 10^7 atoms/litre before 1993 and 270 x 10^7 atoms/litre after 1993 is able to reproduce the observed concentration patterns in 1992 and 1995 (Fig. 4b).

Acknowledgements

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THREE DIMENSIONAL SIMULATION OF RADIONUCLIDES DISPERSION IN THE STRATIFIED ESTUARIES

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Abstract

THREE-dimensional model of TOXicants transport (THREETOX) was developed for assessment of potential and real emergency situations in the coastal area of seas and the inland water bodies. It includes the high resolution numerical hydrodynamic submodel, dynamic-thermodynamic ice submodel, submodels of suspended sediment and radionuclide transport. The results of two case studies are described. The first one concerns to two-year simulation of the Chernobyl origin radionuclide transport through Dnieper-Bug estuary into the Black sea. In the second case study the simulations were performed for the assessment of potential emergency situation caused by the radionuclide release from reactors and containers with the liquid radioactive wastes scuttled in the Novaya Zemlya fjords (Tsivolki, Stepovogo and Abrosimov). The presented results demonstrate the capability of THREETOX model to describe the wide spatial and temporal range of transport processes in the coastal area of seas.

1. INTRODUCTION

The use of computational fluid dynamics models is important for operative forecasts of pollutant dispersion in coastal waters and emergency preparedness and response in the case of accidental industrial releases. Complicated dynamics of the estuaries that is governed by freshwater inflow, wind, tides, sea level variations makes it necessary to use the models that take into account all these factors in the radionuclide transport processes. An advanced THREE - dimensional model of TOXicants transport (THREETOX) was recently developed [1] for the prediction and re-analysis of the pollution transport in the coastal areas of seas and inland water bodies. A brief description of the model is presented in the paper. Two case studies are considered: a two-year simulation of the 1986 accidental Chernobyl radionuclide contamination of the Dnieper-Bug estuary, and a multiyear simulation of a situation caused by a potential radionuclide release from scuttled reactors, and containers with the liquid radioactive wastes, in the Novaya Zemlya fjords.

2. MODEL

The THREETOX code includes a set of submodels.

Hydrodynamics submodel. The hydrodynamics is simulated on the basis of the three-dimensional, time-dependent, free surface, primitive equation model. The prognostic variables of the hydrodynamics code are the three components of the velocity, temperature, salinity and surface elevation.

Ice submodel. The submodel was used to simulate seasonal cycle of moving ice in the seas of temperate zone. The submodel describes the momentum balance, the ice rheology, the mass balance and the ice strength. The ice thickness distribution is a two-level representation that considers the compactness and the mean ice thickness, averaged over an entire grid cell.

Suspended sediment transport submodel. The suspended sediment transport is described by the advection-diffusion equation, taking into account the fall velocity of the sediment grains. The bottom boundary condition describing sediment resuspension or deposition depends on the ratio between equilibrium and actual near bottom suspended sediment concentrations. The thickness of upper (movable) layer of sediments is governed by the equation of the bottom deformation.

Radionuclide transport submodel. The equations of radionuclide transport govern the radionuclide concentration in solute, in the suspended sediments and in the top layer of the bottom deposits. The exchanges between these variables are described as adsorption-desorption and sedimentation-resuspension processes. Three - dimensional advection -diffusion equations are used to simulate the radionuclide transport in the water column and an ordinary differential equation is applied to simulate the concentration of a radionuclide averaged over the thickness of an upper, mobile layer of bottom deposits.

3. CASE STUDIES

3.1. Dnieper-Bug Estuary

The Dnieper-Bug Estuary (DBE) located on the north-west coast of the Black Sea, is the sea's largest estuary, with a surface area of 1006,3 km^2, and a volume of 4.24 km^3. The Estuary is connected with the Black Sea through the Kinbourn strait. The regime of this drowned-river estuary varies from stratified to partially mixed. The sources of fresh water discharge are the Dnieper and Southern Bug rivers. The DBE is the end of the radionuclide riverine transport from the Chernobyl accident area to the Black Sea. The radioactive contamination of the DBE offered the opportunity to study the behaviour of dissolved and particulate substances in the transition zone between fresh and salty aquatic systems. The dynamics of ^{137}Cs and ^{90}Sr in the Dnieper- Bug Estuary and in the adjacent shelf area of the Black Sea was simulated over two years after the Chernobyl accident. The monthly averaged concentrations of the sediment, radionuclide in solute and radionuclide adherent to the sediment in the Dnieper and Southern Bug mouth, were prescribed from May 1986, to April 1988 using the data of [2-4]. At the open sea boundary the concentrations of ^{137}Cs and ^{90}Sr were prescribed according to [5]. In Fig. 2 the measured concentrations of dissolved ^{137}Cs [2] at the surface and in the near bottom layer are compared with the simulated concentrations of the radionuclide along the A-A cross-section in Fig. 1. The data are represented in nondimensional units in order to make it possible to compare results from different years. The variations of dissolved radionuclide concentrations C from the averaged along the DBE concentration $\overline{C}$ were normalised to the maximum difference in radionuclide concentrations along the DBE ΔC. A reasonable agreement of the simulated data with the available measurements was obtained. Discrepancies between the observed [4] and simulated distribution of ^{90}Sr do not exceed the range of the exchange parameters, boundary and initial values uncertainty (see Fig. 3). There was a marked distinction between simulated radionuclide fluxes of ^{137}Cs and ^{90}Sr through the Kinbourn strait. The net flux of ^{137}Cs was much less than the influx and the outflux. In the period covered by the simulation the net flux of ^{137}Cs was directed predominantly towards the Black Sea.. Only at small river influx the net flux of ^{137}Cs was directed to DBE. . The outflux of ^{90}Sr from DBE also dominated throughout year. Calculations showed that more than 90 % of the total inventory 0.72 TBq of ^{137}Cs in DBE in the spring of 1988 was deposited in the bottom sediments while 76% of the total inventory 1.3 TBq of ^{90}Sr was in the solute. The outflux of ^{137}Cs from the DBE during May 1986 - April1988 was found to be equal to 0.67 TBq, that is 48 % from the total input 1.39 TBq. The outflux of ^{90}Sr was equal to 15.5 TBq, that is 92 % from the total input 16.8 TBq. More detailed description of the results of the simulation of radionuclides dispersion in the DBE are presented by [6].

3.2 Novaya Zemlya fjords

The consequences of the possible leakage from the nuclear reactors and containers with liquid wastes that have been scuttled in the Novaya Zemlya fjords and in the Kara Sea in the Novaya Zemlya

Depression (NZD) during the period 1960-1991 have been intensively studied last years by the international groups of the

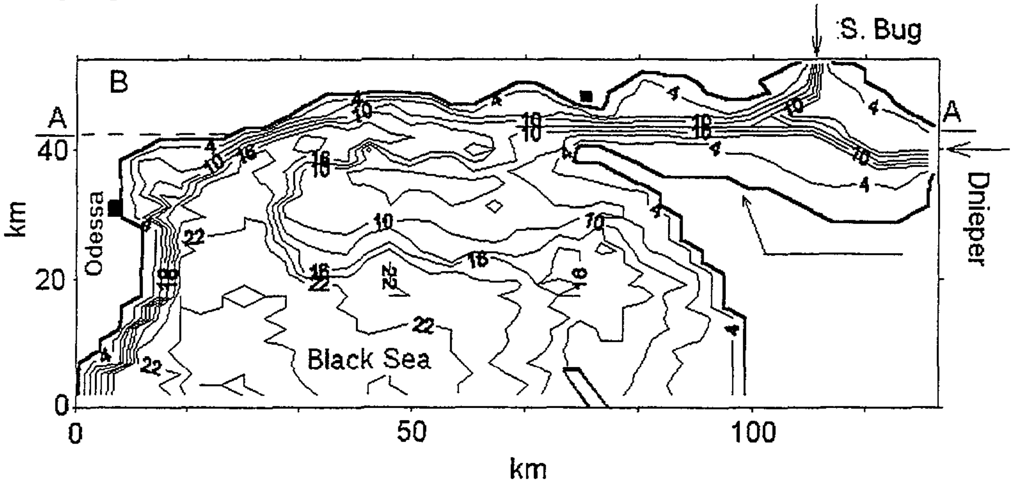


FIG.1 Bottom topography of the Dnieper-Bug Estuary area.

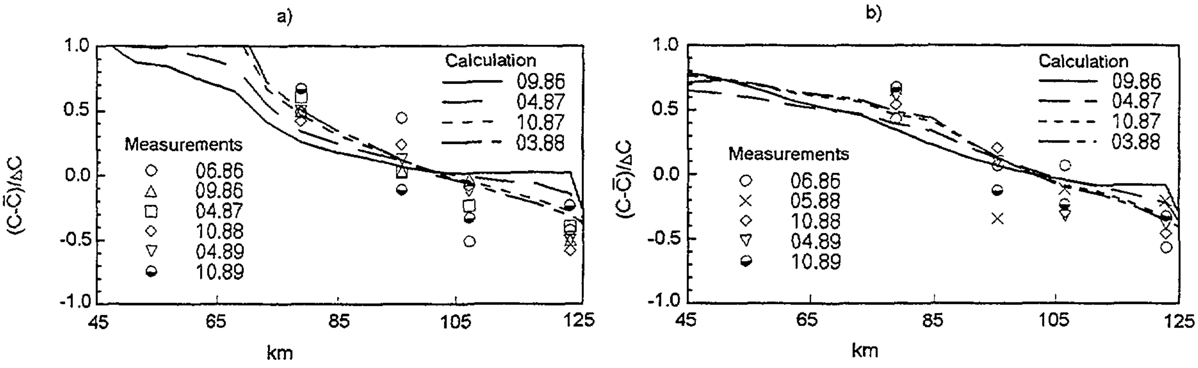


FIG. 2 Computed [6] vs. measured [2] distribution of dissolved ^{137}Cs along the A-A cross-section of DBE and sea shelf in 1986-1989. (a) surface layer; (b) near bottom layer.

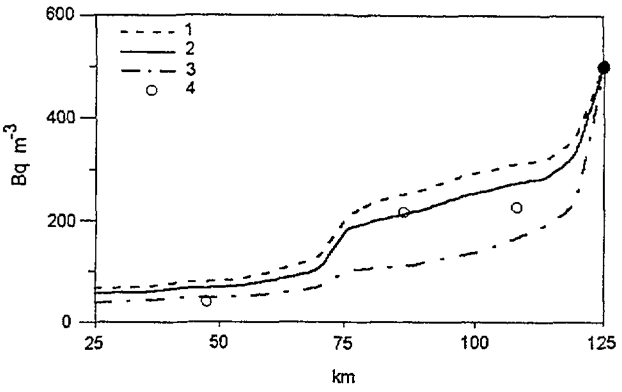


FIG. 3 Computed [6] vs. measured distribution of dissolved ^{90}Sr in the surface layer in March 1988. Circles are data [3] filled circle - [4]. Curve 1 - K_{db}=0; 2 - K_{db}=3.0 m^3/kg; 3 - K_{db}=5.0 m^3/kg, where K_{db} is the coefficient of radionuclides' equilibrium distribution in the "solute-bottom sediments"

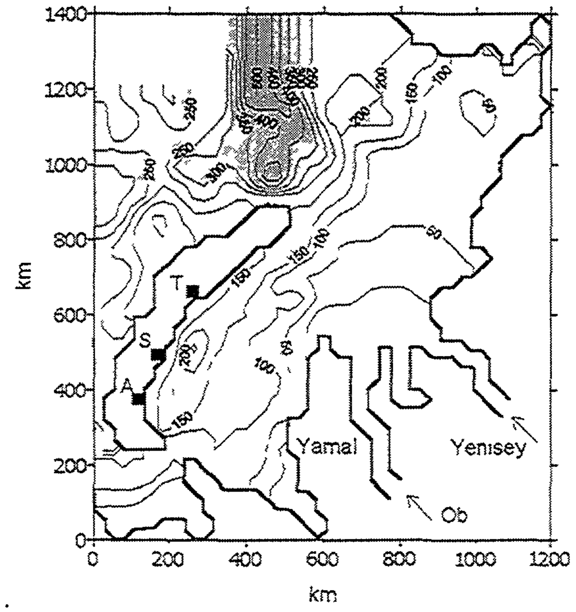


FIG. 4. Bathymetry of the Kara Sea "A" Abrosimov fjord, "S" Stepovogo fjord, "T" Tsivolki fjord

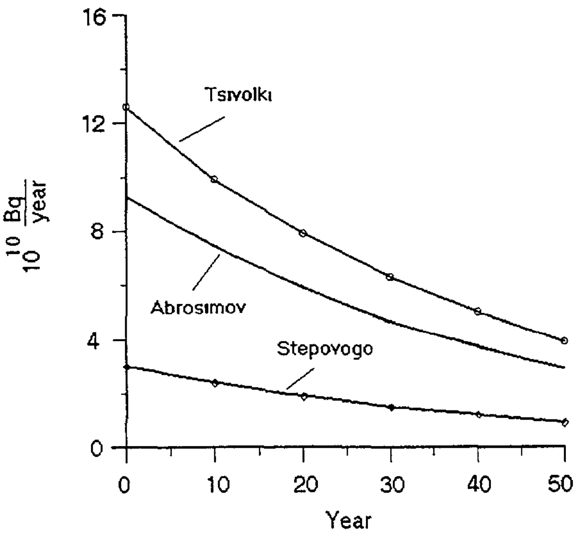


FIG. 5. Scenario or ^{137}Sr release from dump sites in the Novaya Zemlya fjords [8].

experts (e.g., [7]). The recent study [8] was focused on the radiological consequences of the release to man. The radiological collective dose calculations were carried out on the basis of the marine radionuclide concentration values predicted in the long-term projection by the box model [8]. The parameterisation of the water and radionuclide fluxes from the Novaya Zemlya bays required more insight in the hydrodynamic and radionuclide transport processes in the fjords. All these processes were considered in the presented in this paper modelling study, that was provided as a part of the European Commission project [8]. The local scale modelling was performed for dump sites in three fjords (Abrosimov, Stepovogo and Tsivolki). Two years of the radionuclide (^{137}Cs and ^{239}Pu) dispersion were simulated for the potential releases. Information on the fjords has been obtained from the cruise reports [7]. The scenarios of the release of ^{137}Cs in the fjords [8] are given in Fig. 5. According to these scenarios the continuous release will begin from 2050. Strong seasonal effects on the circulation in the fjords caused by summer run-off from a snow melting, and winter ice sheets, in addition to wind and semidiurnal tides were shown in calculations. Let us consider as an example the Stepovogo fjord with the east-west spacing about 9 km and north-south spacing of 3.6 km (Fig. 6). A summer fresh water discharge from the western part of the basin results in the strong water stratification. The halocline depth at summer is about 15-30 m with the salinity variation of 15 ‰ [7]. The nuclear submarine NS 601 was dumped in the relatively shallow channel near the bay mouth. The distribution of ^{137}Cs in the Stepovogo fjord in summer and winter is shown in Fig. 7. The release rate of ^{137}Cs from this fjord is presented in Fig. 8. As shown in Fig.7a, the vertical distribution of ^{137}Cs in the August is inhomogeneous. The concentration of ^{137}Cs in the mouth increases to the surface whereas in the inner part of the fjord it is maximal near the bottom. It can be explained by the seasonal specifics of the tracer transport in the stratified fjords. At winter the outflux of the radionuclides is relatively weak because the ice covers the fjord (Fig.8). It is governed by semidiurnal tides. An influx of fresh water in July-August "pushes" the contaminated water of the upper layer to the fjord mouth. It corresponds to first maximum *F* in Fig. 8. Then flux of more clear water in the upper layer drastically reduced the outflux of ^{137}Cs in Fig.8. In the bottom layer the water flows from the sea and transports radionuclide to the inner part of the fjord. Here the contaminated water rises in the upper layer. A secondary maximum of outflux *F* in Fig. 8 took place while this water found its way to the bay mouth.

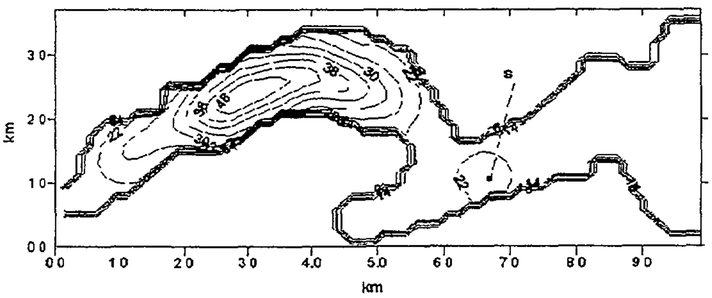
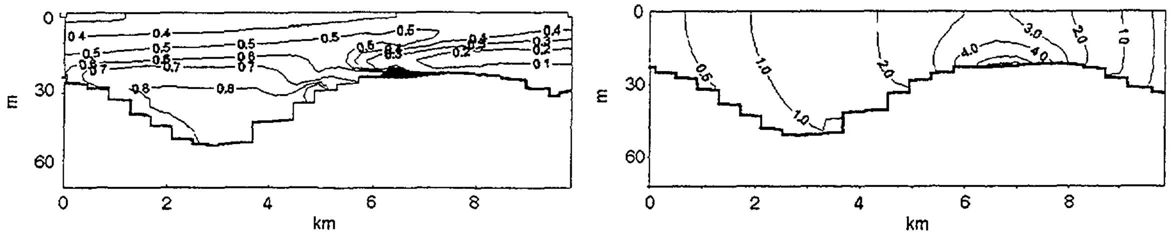


FIG. 6. Bathymetry of the Stepovogo fjord [7].



(a) (b)

FIG.7. Vertical cross-section of ^{137}Cs distribution in the Stepovogo fjord at summer(a) and winter (b) after half and one year since the beginning of a release, respectively.

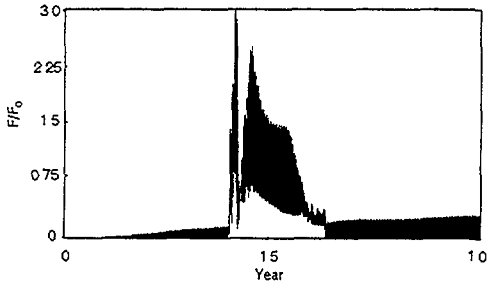


FIG. 8. The release rate of ^{137}Cs from the Stepovogo fjord F normalised to the source release rate F_0. Calculations were made by THREETOX.

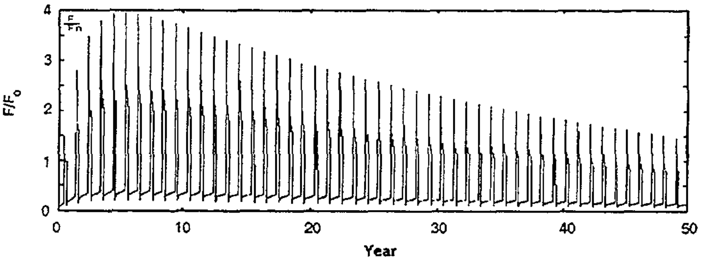


FIG. 9. The release rate of ^{137}Cs from the Stepovogo fjord F normalised to the source release rate F_0. Calculations were made by the box model.

TABLE. I THE OUTFLUX OF ^{137}CS FROM FJORDS AND NOVAYA ZEMLYA DEPRESSION CALCULATED BY THE BOX MODEL (×10^{10} BQ/YEAR)

Year	Outflux from Abrosimov	Outflux from Stepovogo	Outflux from Tsivolki	Source release in NZD	Total source release	Total flux into the Kara Sea
2051	0.4	1.0	3.3	2.2	26.9	6.9
2055	2.1	2.5	9.7	2.0	24.2	16.3
2060	3.3	2.3	9.9	1.7	21.4	17.2
2065	3.9	2.1	9.0	1.6	19.2	16.6
2070	4.1	1.9	8.0	1.4	17.1	15.4
2080	3.8	1.5	6.3	1.1	13.5	12.7
2100	2.8	0.9	3.9	0.7	8.3	8.3

The calculated flushing times ranged from 0.3 months (summer) to 3.4 months (winter) in the relatively small Stepovogo fjord, to 0.6 and 6.0 months for summer and winter, respectively, in the large Tsivolky fjord. Based on the THREETOX estimates of the flushing times, a simple box model for the fjords was developed to extrapolate the results of the 3-D simulation from a few years to the fifty years. The calculated by the box model release rate is given in Fig. 9. This model predicts that the average concentration of ^{137}Cs in the water of fjords didn't exceed 80 Bq m^{-3} (Abrosimov). The box model predicted that, after 50 years since the beginning of a release, the residual amount of the ^{137}Cs in the fjords is about 3 % from the total input. The results of computation are summarised in Table 1. The maximum of the total influx in the Kara Sea is attained after 10 year of the release. The simulation of the radionuclide transport in the Kara Sea was done by THREETOX [8, 9] on the basis of these estimates. It was shown that the marine radionuclide concentration due to the releases are much less than the present day concentration.

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MEAD - THE DEVELOPMENT OF A LONG-TERM DISPERSION MODEL FOR SHELF SEAS

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Abstract

A long-term marine dispersion model, MEAD (Marine Environment Annual Dispersion), has been developed from the CUMBRIA model created by AEA Technology, UK. MEAD includes improvements made to the parameterisation of some of the physical processes represented in CUMBRIA together with a new flowfield and model grid. Transport of pollutants (in this case radionuclides) in the model is defined to occur in three phases; dissolved in the water column and attached to suspended and deposited sediments. A spatially varying suspended particulate material (SPM) concentration field is included in MEAD and ionic exchange between the dissolved and deposited phases is parameterised. Initial comparisons of MEAD results with limited available observed data show good agreement indicating satisfactory representation of the physical processes by the model.

1. INTRODUCTION

The Marine Environment Annual Dispersion (MEAD) model has been developed from the CUMBRIA model, a long-term dispersion model currently used by Westlakes Scientific Consulting Ltd to estimate distributions of radionuclides in the Irish Sea. Both models use annually averaged advection-diffusion equations to represent residual transport of pollutants in the marine environment. The development of MEAD from CUMBRIA has improved the parameterisation of some of the physical processes represented by both models. Unlike the CUMBRIA model, which was specifically designed to model dispersion in the Irish Sea, MEAD is a generic model which can be used to simulate radionuclide transport in any shelf sea area.

2. MODEL FUNCTIONALITY AND STRUCTURE

MEAD is a shelf seas dispersion model designed to simulate the long-term movements of pollutants in the marine environment. Both radionuclides and heavy metals can be simulated and any shelf sea area can be modelled as long as the required initialisation data is provided. Only radionuclide dispersion is considered in this paper.

The model runs in two distinct stages. Stage 1 involves a 100 year simulation of the dispersion of the chosen radionuclide after a unit release (of 10^{12} Bq) during the first year of the simulation period. The cumulative concentrations of the chosen radionuclide, in each phase, are calculated in Stage 2 by combining the normalised results from Stage 1 with a given discharge time series.

2.1. Stage 1

It is assumed that transport of chemicals in the marine environment can take place in three phases: dissolved in the water column, attached to suspended sediment and attached to deposited sediment. Mathematically, dispersion in the three phases is described in MEAD by the equations

$$\frac{\partial hC_1}{\partial t}=-\frac{\partial(hUC_1)}{\partial x}-\frac{\partial(hVC_1)}{\partial y}+\frac{\partial}{\partial x}\left(hK_x\frac{\partial C_1}{\partial x}\right)+\frac{\partial}{\partial y}\left(hK_y\frac{\partial C_1}{\partial y}\right)$$
$$+h\alpha C_2+h\alpha C_3-h\left(K_D\left(\alpha\frac{P}{\rho}+\alpha\frac{l_s\rho_s\phi}{h\rho}\right)+\delta\right)C_1 \tag{1a}$$

$$\frac{\partial hC_2}{\partial t}=-\frac{\partial(hUC_2)}{\partial x}-\frac{\partial(hVC_2)}{\partial y}+\frac{\partial}{\partial x}\left(hK_x\frac{\partial C_2}{\partial x}\right)+\frac{\partial}{\partial y}\left(hK_y\frac{\partial C_2}{\partial y}\right)$$
$$+h\alpha K_D\frac{P}{\rho}C_1+h\frac{w_sP}{L\phi\rho_s}C_3+h\sigma-h\left(\alpha+\frac{w_s}{h}+\delta\right)C_2 \tag{1b}$$

$$\frac{\partial hC_3}{\partial t}=h\alpha K_D\frac{l_s\rho_s\phi}{h\rho}C_1+h\frac{w_s}{h}C_2-h\left(\alpha+\frac{w_sP}{L\phi\rho_s}+\delta\right)C_3 \tag{1c}$$

where

C_1	is the depth-averaged dissolved phase radionuclide concentration (Bq m^{-3}),
C_2	is the depth-averaged suspended phase radionuclide concentration (Bq m^{-3}),
C_3	is the depth-averaged deposited phase radionuclide concentration (Bq m^{-3}),
h	is the mean water depth (m),
U,V	are perpendicular components of the residual velocity field (m s^{-1}),
K_x,K_y	are perpendicular components of the coefficient of dispersion (m^2 s^{-1}),
α	is the desorption rate (s^{-1}) (set to 7.7×10^{-4} s^{-1}),
K_D	is the partition coefficient,
P	is the annual mean suspended particulate material (SPM) concentration (ppm),
w_s	is the mean settling velocity (m s^{-1}) (set to 2.5×10^{-5} m s^{-1}),
δ	is the decay constant (s^{-1}),
ρ,ρ_s	are the water and sediment deposit densities, respectively (kg m^{-3}) (set to 1000 and 1500 kg m^{-3}, respectively),
l_s	is the bed desorption depth (m) (set to 0.01 m),
L	is the bed mixing length (m) (set to 0.4 m),
ϕ	is the percentage of mud in the bed sediment deposit,
σ	is a source term (Bq m^{-3} s^{-1}).

Equations (1a) and (1b) are depth-averaged advection-diffusion equations with source and sink terms represented by the transfers between different phases. Equation (1c) has no advective/diffusive components since bed sediment is not transported directly (it can, however, be transported indirectly through resuspension and movement in the suspended phase).

The dispersion coefficients K_x and K_y used in the model take into account both tidal stirring and diffusion and are calculated by the formulae [1]

$$K_x=a_1u_0\sqrt{\left(u_0{}^2+v_0{}^2\right)}+\frac{h^2\sqrt{\left(U^2+V^2\right)}}{a_2K_z}\left(|U|+\frac{|V|}{a_3}\right)$$
$$K_y=a_1v_0\sqrt{\left(u_0{}^2+v_0{}^2\right)}+\frac{h^2\sqrt{\left(U^2+V^2\right)}}{a_2K_z}\left(\frac{|U|}{a_3}+|V|\right)$$

where u_0 and v_0 are the x- and y-components of the mean tidal amplitude, a_1, a_2 and a_3 are constants and K_z is the vertical diffusion coefficient.

Transfer between the suspended and dissolved phases is represented by the desorption rate and transfer between dissolved and suspended phases (adsorption) is defined by the formula

$$\alpha K_D \frac{P}{\rho}$$

where the affinity of the radionuclide to adsorb onto sediment is represented by the partition coefficient, K_D, which is defined to be the ratio

$$K_D = \frac{\text{activity per unit weight of sediment}}{\text{activity per unit weight of seawater}}$$

and is different for each radionuclide. Adsorption to the deposited phase from the dissolved phase is defined by the formula

$$\alpha K_D \frac{l_s \rho_s \phi}{h\rho} \qquad (2)$$

where the bed desorption depth is defined to be the depth from which radionuclides bound to the bed sediment can desorb.

Transfer between suspended and deposited phases occurs through sediment deposition and this is calculated using an average settling velocity. Resuspension of the bed sediment accounts for transfer between the deposited and suspended phases and is governed by the resuspension rate

$$\frac{w_s P}{L \rho_s \phi}$$

Since MEAD deals with long-term simulations, it is assumed that only the mud in the bed sediments contributes to the net resuspension (since sand and larger particles are eroded and deposited over relatively short periods). The resuspension rate is thus defined to be related to the spatially varying percentage of mud on the sea bed and the local SPM concentration as well as the density of the sediment deposit and the estimated mixing depth of the bed.

Equations (1a), (1b) and (1c) are solved in Stage 1 of the model by using finite differences to discretise the equations over a regular grid and applying a version of Gear's method of solution for a system of ordinary differential equations [2].

2.2. Boundary conditions

The open boundaries of the grid, which allow flow though them, require coefficients which describe how the simulated radionuclide behaves at them. There are a maximum of four open boundaries in each grid: northern, eastern, southern and western. A radionuclide concentration gradient, which may vary along the boundary, is defined across each of the boundaries present in the grid area. The radionuclide concentration gradients across the open boundaries which are used in the model are determined to be those that give the best fit to available observed data.

2.3. Stage 2

The normalised radionuclide concentrations for each year of the 100 year period simulated in Stage 1 are used by Stage 2 of MEAD. The effects of a historical discharge record can be modelled or the long-terms effects of a projected new discharge can be estimated, depending on the type of discharge data supplied. The cumulative radionuclide concentrations, C_C, in year X of the 100 year simulation period are calculated by combining the supplied discharge data and the results of Stage 1 of the model using the formula

$$C_C = \sum_{j=1}^{X} C_{X+1-j} D_j$$

where C_j is the normalised radionuclide concentration in the jth year of the Stage 1 simulation (Bq m^{-3}) and D_j is the amount discharged in the jth year of the Stage 2 calculation period.

3. MODEL DEVELOPMENT

MEAD was developed from the CUMBRIA model, created by AEA Technology [3]. Conclusions drawn from early validation attempts of the CUMBRIA model [4] indicated that the physical basis of the model could be improved to make the simulated annual mean radionuclide concentrations more realistic.

3.1. New grid and flowfield

The development of MEAD as a new model was based on the need for a higher resolution of the Irish Sea area. Figure 1 shows the model grid used by the CUMBRIA model together with the area covered by the new grid used by MEAD (indicated by the dashed line). The resolution of the CUMBRIA grid varies between 1.5 km and 12 km whereas the MEAD grid has a regular resolution of 2 km (the individual cells of the MEAD grid are not shown in Figure 1 due to space restrictions).

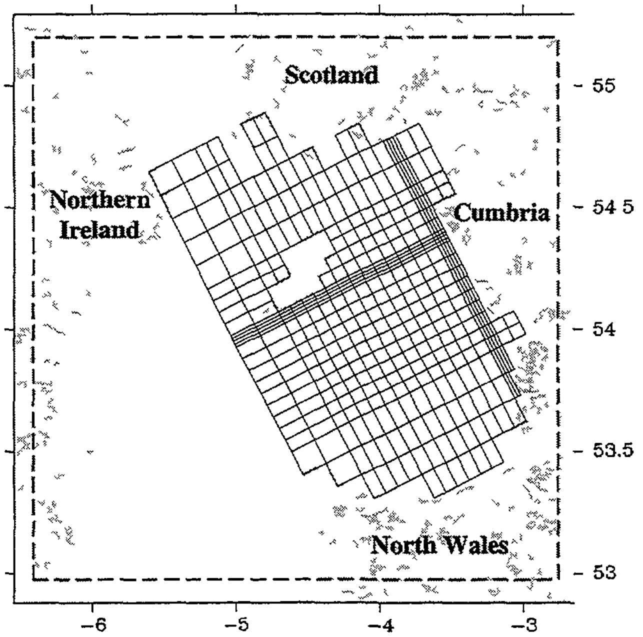

FIG. 1. The CUMBRIA model grid and the coverage of the MEAD grid.

The use of a new grid by MEAD also required that a new residual flowfield be developed. In the CUMBRIA model, the flowfield was defined as a streamfunction, which was interpolated from data produced by a hydrodynamic model with a 35 km resolution grid. MEAD has been developed to use residual velocities produced by running the MIKE21 tidally resolving model (developed by the Danish Hydraulics Institute) using the same 2 km resolution grid as that used by MEAD. The use of a generic hydrodynamic model such as MIKE21 allows a residual flowfield for MEAD to be applied to any shelf sea area.

3.2. SPM Concentration Field

The main area of improvement to physical process representation in MEAD, compared with CUMBRIA, has been in the definition of the SPM concentration field. In the CUMBRIA model, the SPM concentration field in the Irish Sea was defined to be a spatially invariant 4 mg l^{-1}. In reality, SPM concentrations vary from an annual average of ~ 2 mg l^{-1} in deeper regions to ~10 mg l^{-1} in coastal regions, such as Liverpool Bay [5]. A long-term suspended sediment transport model has been developed, based on MEAD, so that an annual mean SPM concentration field could be derived for use in MEAD. Annually averaged resuspension and deposition terms, based on tidal amplitudes, are used and advection and diffusion of suspended sediments is simulated using the same residual flowfield as used by MEAD. Figure 2 shows the SPM concentrations (observed and simulated) in a line across the Irish Sea at 53°40'N.

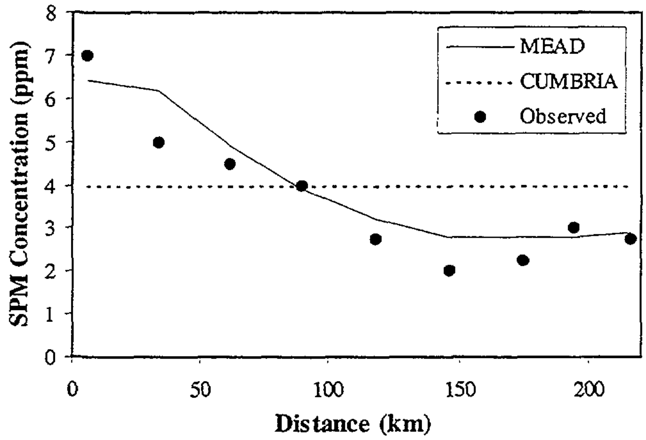

FIG. 2. Observed annual mean SPM concentrations [5] and values used in both CUMBRIA and MEAD. Distances are given in km from the English coast.

3.3. Ionic exchange with the deposited phase

A proportion of long-lived radionuclides discharged into marine environments becomes attached to sediment that ultimately resides in the seabed. Studies [6] have shown that a significant proportion of dissolved phase radioactivity results from desorption of radionuclides from the seabed, this being especially true for caesium. The seabed is thus a source of radioactivity to the seawater and is becoming increasingly important as long-lived radionuclides that reside in fine-grained seabed sediments are returned to the sediment surface [7]. As such, the ionic exchange process between seabed sediment and seawater must be included in any model describing the transport of radionuclides.

This process was not included in CUMBRIA, however, a parameterisation of ionic exchange with deposited sediment, based on that used to represent ionic exchange with suspended sediment, was developed for use in MEAD. Exchange between the deposited fine-grained sediment and the water column is governed by the desorption rate, α, detailed in Section 2.1. The adsorption of radionuclides onto fine-grained deposited sediment from the dissolved phase is represented in MEAD by the formula (2) given in Section 2.1.

4. INITIALISATION DATA

The data required to run MEAD are a depth array of the model area, the flowfield resolved into two perpendicular components (which is usually derived from running MIKE21 using the same depth array which is supplied to MEAD), a bed mud percentage array and an annual mean SPM concentration array, which is usually derived from running the sediment transport model mentioned in Section 3.2 (which can be accessed from the same platform as MEAD).

5. PRELIMINARY RESULTS

The results shown in Figure 3 are for ^{137}Cs concentrations in the dissolved phase in 1963. Model predictions are compared with annually averaged observations [8] at sites along the Cumbrian coast.

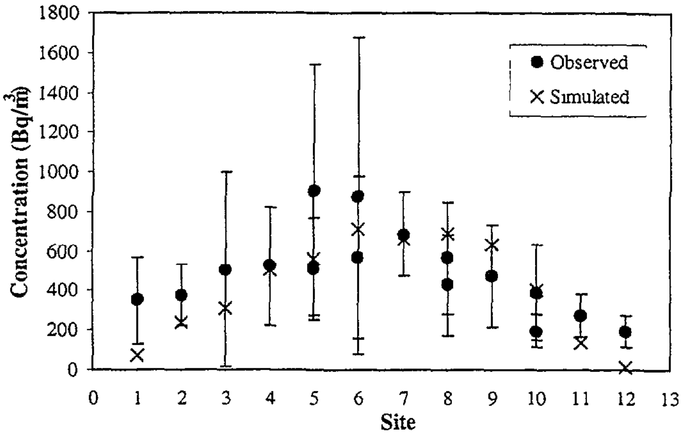

FIG. 3. Model simulated dissolved phase concentrations of ^{137}Cs (dots) compared with annually averaged observed concentrations of ^{137}Cs in filtered seawater (crosses).

The model is still in the early stages of calibration and a subsequent full validation will be carried out however these initial results are very encouraging. The dispersion parameter values which give these results are a_1=0.01, a_2=100, a_3=3 and K_z=1.0×10^{-4}.

6. CONCLUSIONS

An annually averaged marine dispersion model, MEAD, has been developed from an existing model, CUMBRIA, with improvements made to the parameterisations of some of the physical processes represented by the original model as well as the use of a new flowfield. Both ionic exchange with the seabed sediments and a spatially varying SPM concentration field are considered by MEAD whereas CUMBRIA did not include these processes. The new model is currently undergoing a full validation but initial tests of the model results show that MEAD represents the processes in the Irish Sea well and good agreement with observed data is achieved.

Acknowledgements

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A MONTE CARLO APPROACH IN QUALITY ASSURANCE OF GAMMA SPECTROMETRIC MEASUREMENTS OF MARINE SAMPLES

XA9951923

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Abstract

Experience has demonstrated that data reliability in environmental radioactivity assessments is best achieved by a well designed quality assurance programme. A special attention has been devoted to gamma-spectrometric measurements of marine samples. Detector calibration, matrix corrections and coincidence corrections for large volume semiconductor detectors were carefully considered by means of realistic Monte Carlo simulations. The ISO-IUPAC recommendations for uncertainty estimation were followed in order to have a correct estimate of the uncertainty budget for each radionuclide analysis.

1. INTRODUCTION

Improvements in environmental radioactivity assessments are heavily dependent on reliable data resulting from complex measurement processes. A quality assurance programme which comprises quality control and quality assessment procedures leads to the production of reliable data. Experience has demonstrated that data reliability is best achieved by a well designed quality assurance programme.

Special attention was paid to analytical methods, especially to gamma-spectrometry. Low level gamma-spectrometry is one of the most important analytical methods covering a wide range of measurements going from routine environmental surveys to fundamental research.

In the present paper we concentrate on those aspects of quality management which may be introduced during gamma spectrometry of marine samples.

A Monte Carlo method to compute the efficiency of coaxial and well-type HPGe detectors has been developed. Self-attenuation and coincidence corrections have been introduced as well using specific software. Also a systematic procedure to compute uncertainties in gamma-spectrometric measurements, as well as the combined standard uncertainty has been developed .

2. QUALITY ASSURANCE IN GAMMA-SPECTROMETRY

Quality assurance consists of the establishment of techniques to control quality (quality control) and techniques to evaluate their effectiveness (quality assessment). The basic elements of quality control are: good laboratory practices (GLPs), standard operations procedures, protocols for specific purposes and training. Quality assessment techniques denote those ways in which the measurement process may be monitored in order to infer the quality of the data output. The methods used are classified as internal or external, depending on the sources of assistance needed to implement the assessment technique.

Measurement data must be technically sound and often must be legally defensible. Adequate documentation is a key requirement in all aspects of quality assurance.

Taking into account the importance of environmental data in economic, ecological and legal decision-making, IAEA-MEL has reviewed the actions which should be taken to assist laboratories in improving data quality. In particular it has been proposed that the IAEA's Analytical Quality Control Services (AQCS) programmes should address in full the complex problem of total quality management of analytical laboratories, including provision of quality assurance programmes and manuals, organization of intercomparison exercises with proper feedback, development of reference methods, production of certified reference materials (CRMs) and training in quality assessment and control [1,2].

Special attention was paid to the gamma-spectrometric measurements of marine samples. Gamma-spectrometry is recognized as a wide-purpose multi-nuclide method of analysis presently based mainly on the use of high resolution semiconductor detectors of planar, coaxial or well type. In order to improve the quality of gamma-spectrometric results, IAEA-MEL has implemented high-efficiency measuring systems using well-type (150% relative efficiency) and coaxial HPGe detectors (100% and 170 % relative efficiencies). The matrix corrections and the coincidence corrections were carefully considered for the new high efficiency detectors by means of realistic Monte Carlo simulation method using the GESPECOR algorithm and software [3].

In order to reduce the experimental effort and to improve the accuracy of efficiency calibration, Monte Carlo simulation is an attractive means because any source-detector configuration and any sample matrix can be modelled over the energy interval of interest.

3. EFFICIENCY CALCULATION FOR SEMICONDUCTOR DETECTORS USING MONTE CARLO SIMULATIONS

We suppose that detector response has axial symmetry, and the effects resulting from incomplete charge collection can be neglected. The full peak efficiency $\varepsilon(E)$ of the detector for photons of the energy E emitted from a sample of the total linear attenuation coefficient μ is given by the ratio of the number of photons which have lost their full energy in the sensitive volume of the detector and the total number of photons emitted from the sample in the same period of time. Let $w_\mu(\bar{r},\Omega,E)\,dV\,d\Omega$ be the probability for such a photon (with energy E) emitted from the volume element dV at $\bar{r}$ in the solid angle $d\Omega$ to be registered in the full energy peak:

$$\varepsilon_\mu(E) = \frac{1}{4\pi V}\int_V\int_{\Omega(\bar{r})} w_\mu(\bar{r},\Omega,E)\,dV\,d\Omega$$

with

$$w_\mu(\bar{r},\Omega,E) = \exp(-\mu\, l(\bar{r},\Omega))\; T(\bar{r},\Omega,E)\; p_i(\bar{r},\Omega,E)$$

where the first term gives the attenuation effects in the sample and $l(\bar{r},\Omega)$ expresses the length of the photon trajectory through the sample. $T(\bar{r},\Omega,E)$ accounts for photon attenuation in the container walls, the detector end cap and germanium dead layers and $p_i(\bar{r},\Omega,E)$ is the probability of registration in the full energy peak of a photon that enters into the sensitive volume of the detector.

The probability of photon interactions in germanium detectors is computed on the basis of polynomial expressions and the Compton effect is modelled as in the Wielopolsky and Arinc algorithm [4]. Triplet production and positron anihilation in flight are neglected. Secondary electrons are simulated with a condensed history scheme, based on the Bethe-Moliere theory. The computation of efficiency based on the above mentioned formula can be conveniently evaluated by the Monte Carlo method.

The result of Monte Carlo calculation of the detector efficiency is shown in Fig.1 (for the detector of 100 % relative efficiency). A comparison with a traditional polynomial interpolation procedure shows that the Monte Carlo method gives by a factor of 2 smaller uncertainties in the estimation of the detector efficiency.

4. MATRIX AND COINCIDENCE CORRECTIONS

4.1 Matrix corrections

Ideally, the calibration of each measuring geometry should be carried out by using a variety of calibration sources to reproduce the specific photon attenuation effects in each type of sample measured. Because in practice this is almost impossible, the dependence of the full energy peak

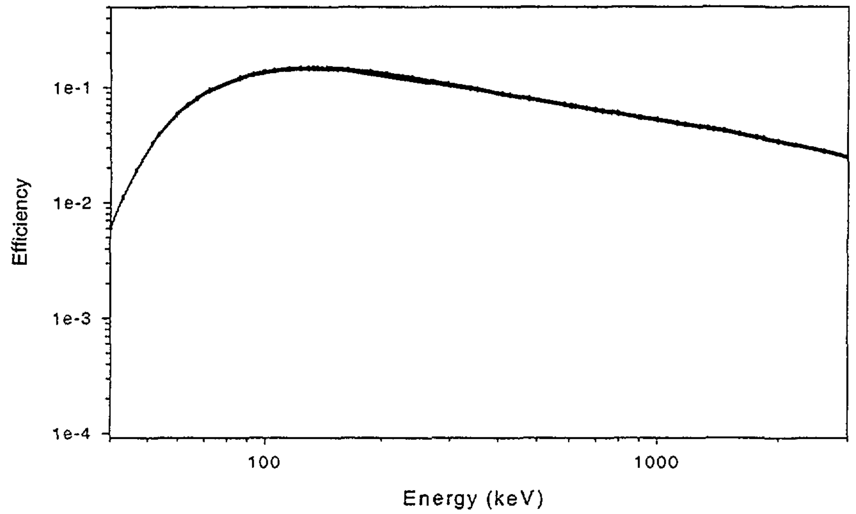

FIG. 1 Monte Carlo calculation of the detector efficiency (coaxial HPGe detector of 100% relative efficiency; marine sediment 3.95cm, thickness 1cm)

efficiency on the density and composition of the sample (the matrix effects) should be evaluated by specific methods.

The methods based on analytical expressions are approximate, either neglecting detector characteristics, or being restricted to weak self-attenuation. Semi-empirical methods may provide better results, but generally require additional experimental work. On the other hand Monte Carlo simulations can be successfully applied to compute these corrections for any geometry and sample matrix.

The self-attenuation factor $F_a(\mu)$ which is a measure of efficiency reduction due to the self-attenuation in the sample is defined as:

$$F_a(\mu) = \frac{\varepsilon(\mu, E)}{\varepsilon_0(E)}$$

where $\varepsilon(\mu, E)$ is the detection efficiency (the full energy peak) corresponding to the energy E and the linear attenuation coefficient μ of the sample, and $\varepsilon_0(E)$ is the corresponding detection efficiency for the same energy E and μ=0.

The self-attenuation factor is then given by the following expression[5]:

$$F_a(\mu) = \frac{\int_V dV \int_{\Omega(\bar{r})} d\Omega N(\bar{r}) \exp^{-\mu l(\bar{r},\Omega)} T_a(E,\bar{r},\Omega) p_i(E,\bar{r},\Omega)}{\int_V dV \int_{\Omega(\bar{r})} d\Omega N(\bar{r}) T_a(E,\bar{r},\Omega) p_i(E,\bar{r},\Omega)}$$

where:

$N(\bar{r})dV$ is the emission rate of photons of energy E from the volume element dV, $\bar{r}$ and Ω are the intitial coordinate and direction of flight of the photon, $l(\bar{r},\Omega)$ is the photon path length through the source, $\exp(-\mu l(\bar{r}, \Omega))$ is the probability of non-interaction in the sample for the photon emitted from point $\bar{r}$ and direction Ω, $T_a(E,\bar{r},\Omega)$ is the probability of non-interaction in the media interposed between the sample and the sensitive volume of the detector, $p_i(E,\bar{r},\Omega)$ is the probability of registration in the full energy peak of a photon that enters into the sensitive volume of the detector.

The sample composition and density are completely characterized by the value of attenuation coefficient μ.

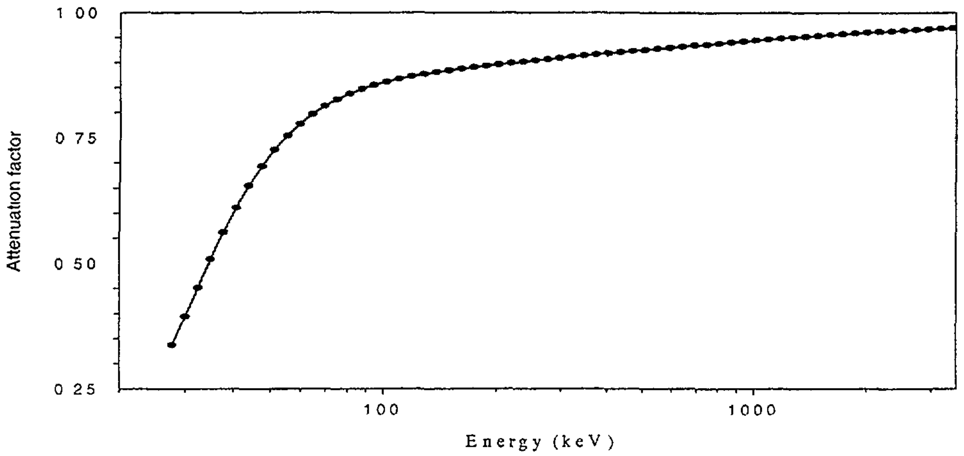

FIG 2. Self-attenuation correction factor versus energy

As an example in fig.2 the energy dependence of the self-attenuation factor is presented for a marine sediment sample with density 1.3 g cm^{-3} instead of water matrix with density 1.0 g cm^{-3}

4.2 Coincidence corrections

Random coincidence summing could appear when two gamma rays interact with detector simultaneously. The probability of such an effect depends on the number of gamma-rays which hit the detector in the unit of time.

True coincidence summing (TCS), or shortly coincidence summing, occurs for radionuclides emitting two or more photons in sequence within the resolving time of the spectrometer. Two fundamental effects can be produced: coincidence losses from the peak and coincidence summing up in the peak. The coincidence-summing effects depend in a complicated way on the decay scheme of the nuclide, on the sample geometry and composition, on the detector efficiency and on the distribution and scattering properties of the materials surrounding the sample and the detector. The coincidence-summing effects depend on the probability that other radiations are emitted simultaneously with the gamma radiation for which the effects are computed.

The coincidence correction factor F_c is defined as the ratio of the apparent efficiency for the energy E of the nuclide with coincidence-summing effects to the efficiency for the same energy derived from the efficiency calibration curve obtained with nuclides with negligible coincidence-summing effects. The correction factor deviates more from 1 in the case of high efficiency detectors, for measurements in geometries close to the detector. The corrections are exceptionally high in the case of measurements performed with well-type detectors.

For nuclides decaying by the emission of photons in cascade, the only way to avoid the necessity of applying coincidence-summing corrections is to make measurements relative to a standard source containing known amounts of activity of the nuclide of interest, in an identical matrix (the same composition and density), measured in exactly the same geometry as the sample under investigation. This is difficult and sometimes impossible.

The other possibility is to estimate the coincidence-correction factor by theoretical computations as discussed previously. The GESPECOR method is a convenient and general method to evaluate both matrix and coincidence corrections based on Monte Carlo simulations. Generally the calculation of coincidence corrections is performed as follows:

-using the decay schemes, for a given radionuclide, the cascade decay probability is determined.

-the full energy peak efficiency for the energies of interest and total detection efficiency are determined.

These values are combined based on specific relations which depend on the decay scheme. The results obtained for coincidence correction factors are presented in Table 1 for the case of HPGe detector (100 % relative efficiency). The shield is included in the computations.

5.. UNCERTAINTY ESTIMATES OF THE MEASUREMENT DATA

Whatever the technique used, it is essential to accompany the result of an experimental measurement by a realistic estimate of the uncertainty of the measurement. The "Guide to the expression of uncertainty in measurement" published by ISO [6] establishes general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurements.

IAEA-MEL has developed a systematic procedure to compute uncertainties in gamma-spectrometric measurements of environmental samples, as well as the combined standard uncertainty [7]. Within this systematic procedure, the overall uncertainty takes into account uncertainties associated with radiochemical separations (when radiochemistry is involved), as well as the uncertainties associated with nuclear data (emission probability, half-life), efficiency calibration procedure, sample preparation, count-rate, self-attenuation and coincidences.

TABLE I. COINCIDENCE CORRECTION FACTORS FOR HPGe DETECTOR (100% RELATIVE EFFICIENCY) AND CYLINDRICAL GEOMETRY WITH R=3.95 cm AND H=1 cm

Radionuclide	Energy (keV)	F_c
Co-60	1173	0.84 ± 0.01
Co-60	1332	0.84 ± 0.01
Cs-134	604	0.82± 0.02
Cs-134	795	0.79± 0.02
Y-88	898	0.86± 0.02
Y-88	1836	0.84± 0.02
Co-57	122	0.99± 0.01
Ag-110m	658	0.69± 0.03
Sb-125	427	0.98± 0.01
Ba-133	81	0.78± 0.04
Ba-133	383	1.08± 0.04
Eu-152	344	0.92± 0.05
Pb-214	53	0.81± 0.02
Pb-214	258	0.79± 0.02
Pb-212	300	0.82± 0.02
Tl-208	583	0.82± 0.01
Tl-208	2614	0.78± 0.01
Ru-106	622	0.81± 0.02

The identification of the sources of uncertainties for each nuclear analytical techniques is an important step. In the case of gamma spectrometry method, Table 2 presents an overview of the most important sources of uncertainties and the magnitude of their contribution. These values are illustrative only. For each practical situation the complete uncertainty evaluation must be done, taking into consideration all possible sources of uncertainties.

The uncertainty is reported as standard uncertainty, combined standard uncertainty or expanded uncertainty[8]. The sources of standard uncertainties can be grouped according to their origin into 3 categories:

-from preparation of test portion,

-from energy and efficiency calibration,

-from the measurement of test portion.

TABLE II. SOURCES OF UNCERTAINTIES

Uncertainty source	Typical uncertainty range (%)	Typical uncertainty value (%)
Counting	0.1 - 20	5
Emission probability	0.1 - 11	< 2
Attenuation correction	0.1 - 5	<1
Coincidence correction	1 - 15	<3
Half-life	0.01 -1	<0.2
Detector efficiency	1 - 5	2
Radiochemical procedures	1-10	3
Sample weight (volume)	0.01- 1	<0.5

The sources of uncertainties which may arise during the preparation of test portion are the following:

-uncertainty due to analyte losses and or contamination,
-uncertainty of sample mass of volumes,
-uncertainty due to sample inhomogeneity,
-uncertainty due to preconcentration procedure.

As a consequence of measurement of test portion the following contribution as uncertainties sources may appear:

-uncertainty due to differences in counting geometries of sample and standards,
-uncertainty due to random coincidences,
-uncertainty due to true coincidences,
-uncertainty due to dead time effects,
-uncertainty due to decay time effects,
-uncertainty due to self-attenuation correction,
-uncertainty due to net peak area determination,
-uncertainty due to counting statistics,
-uncertainty due to half-life,
-uncertainty due to emission probability.

However not all of the uncertainties' components will contribute significantly to the combined uncertainty.

The first step in the quantification is to make a preliminary estimate of the contribution of each component to the combined uncertainty in order to eliminate those that are insignificant.

If the major elements of the sample matrix are known, then the relative uncertainty of the self-attenuation correction factor is less than 1% (for the energy higher than 60 keV) and less than 5% the for energy less than 40keV.

In most cases the quantity of interest (the measurand) cannot be measured directly. Its value has to be derived from values of several other quantities. The activity of the radionuclide (analyte) is a function of other quantities (detector efficiency , gamma ray emission probability, counting rate, corrections factors) where each of these values has an associated standard uncertainty.

The combined standard uncertainty of the quantity of interest (the measurand -y) could be derived by applying the "error propagation law " of Gauss. Thus the combined standard uncertainty of y, $u_c(y)$, is calculated in terms of the component uncertainties.

Most of the algorithms used for efficiency calibration assumed that the true efficiency function can be represented by the fitted analytical function. But the correct allocation of uncertainties to an interpolated efficiency value is a complex problem. The uncertainty of an efficiency value calculated with the interpolation function cannot be obtained only from the uncertainties in the parameters. The possible correlations between the measured input efficiency data must be considered. Also, there are always energy regions where the true efficiency curve systematically deviates from the fitted curve. This systematic difference is only rarely included in the uncertainty computed by the algorithms.

A calculation approach that yields good results is the Monte Carlo method which is based on the simulation of individual photon histories. This is an attractive means because any source-detector configuration and any sample matrix can be modeled over the energy interval of interest. Thus the calculation can provide the shape of the efficiency curve and the efficiency uncertainty at any energy. The uncertainties in the detector data have a much stronger effect on the efficiency than on the self-attenuation factor.

The specific activity A of a gamma emitting radionuclide in the sample, is calculated as

$$A = \frac{N}{\varepsilon \, \gamma \, T_s \, m \, K_1 \, K_2 \, K_3 \, K_4 \, K_5},$$

where N is the corrected net peak area of the corresponding photopeak and the substraction of instrumental background give the corrected net peak area (N) as follows:

$$N = N_s - \frac{t_s}{t_b} N_b,$$

N_s is the net peak area in the sample spectrum,

N_b is the corresponding net peak area in the background spectrum,

ε is the efficiency at photopeak energy,

t_s is the live time of the sample spectrum collection in seconds,

t_b is the live time of the background spectrum collection in seconds,

m is the mass of the measured sample,

γ is the emission probability of the gamma line corresponding to the peak energy,

K_1 is the correction factor for the nuclide decay from the time the sample was sampled to the start of the measurement :

$$K_1 = \exp\left(- \frac{\ln 2 \cdot \Delta t}{T_{1/2}} \right)$$

Δt is the elapsed time from the time the sample was taken to the beginning of the measurement.
$T_{1/2}$ iS half life of radionuclide.
This is useful when there is a long time (relative to the radionuclide half-life) between the sample collection time and the sample count time.
K_2 is the correction factor for the nuclide decay during counting period:

$$K_2 = \frac{T_{1/2}}{\ln 2 \cdot t_r} \left(1 - \exp\left(- \frac{\ln 2 \cdot t_r}{T_{1/2}} \right) \right),$$

t_r is elapsed real clock time during the measurement.
The decay during acquisition correction is used to correct the activity of nuclides whose half-life is short compared to the spectrum real time.
K_3 is the correction factor for self-attenuation in the measured sample compared with the calibration sample. The self-attenuation factor K_3 is defined as the ratio of full energy peak efficiency $\varepsilon(\mu, E)$ for a sample with linear attenuation coefficient μ and the full energy peak efficiency $\varepsilon(\mu_{ref}, E)$ for a sample with linear attenuation μ_{ref}

$$K_3(\mu) = \frac{\varepsilon(\mu, E)}{\varepsilon(\mu_{ref}, E)}$$

If more than one photon is absorbed by the detector during a pulse sampling cycle, the sum of the energies of two (or more) is recorded in the spectrum instead of two (or more) different signals. Any full-energy photon that is summed with another pulse is not recorded in the single photon peak and represents a loss of counts or efficiency. This loss is count rate dependent . K_4 is the correction factor for pulses loss due to random summing [9]:

$$K_4 = \exp(-2\,R\,\tau),$$

where τ is the resolution time of the measurement system and R is the mean count rate. For low count rates this correction factor could be taken as 1.

K_5 is the coincidence correction factor for those nuclides decaying through a cascade of successive photon emissions. If the nuclide has no cascade of gamma-rays then $K_5 = 1$. Also if the calibration sample and measured sample contain the same nuclide then there is no need for this correction ($K_5 = 1$).

The coincidence correction factor K_5 for the line with energy E of the nuclide having cascading radiations is defined as the ratio of the corresponding apparent efficiency $\varepsilon^{ap}(E)$ to the full energy peak efficiency, $\varepsilon(E)$, at the same energy obtained from the energy curve (or Monte Carlo simulation) measured with single-photon emitting nuclides

$$K_5 = \frac{\varepsilon^{ap}(E)}{\varepsilon(E)}$$

K_5 depends on nuclide decay scheme, on sample geometry and composition and on detector parameters.

Detection and quantification capabilities represent fundamental performance characteristics of any measurement processes. In the ISO document [6], detection limits (minimum detectable amounts or activity in our case) are derived from the theory of hypotesis testing and the probabilities of false positives α and false negatives β. Quantification limit (minimum quantifiable value) is defined in terms of a specified value for the relative standard deviation (RSD) of the estimated quantity.

In some particular situation obtaining a rigorous expression for detection limit is problematic. But when the distribution of measured quantity can be taken normal, with constant standard deviation σ_0 and default parameter values for α , β (0.05 each) and RSD then we obtain the simple approximate expressions [10], for the following quantities:

- detection decision (Critical Value), L_c
- detection limit (Minimum Detectable Value), L_D
- quantification limit (Minimum Quantifiable Value), L_Q

Thus for the normal limit of Poisson distribution the following approximate formula for detection limit could be used:

$$L_D \approx \frac{1}{2\eta}(k_\alpha + k_\beta)^2 + (k_\alpha + k_\beta)\sqrt{\eta B}$$

where: k_α = k_β =1.65 for default α= β=0.05, B is the background counts and η (the design parameter) is between ≈ 1 and 2, depending on the ratio of background and sample counting time. If the background estimate has negligible uncertainty then $\eta = 1$ [10].

There are many factors affecting the Minimum detectable Activity (MDA). The efficiency, the sample matrix, the backgrounds (system and source induced) , the detector resolution, the time available for the measurements and the particular nuclide , all substantially affect the MDA reported.

The MDA will also include the correction factors ($K_1 .. K_5$) used for activity calculation, and finaly can be expressed as:

$$MDA = \frac{L_D}{\varepsilon \gamma T_s m K_1 K_2 K_3 K_4 K_5},$$

where :
L_D is the detection limit as described above,
T_s is live time,
ε is the efficiency at photopeak energy,
m is the mass of the measured sample,
γ is the emission probability of the gamma line corresponding to the peak energy
K_i are the correction factors (i=1..5) as described before.

In Table 3 an example of the uncertainty budget computed for ^{60}Co in marine sediment is presented.

6. CONCLUSIONS

Quality assurance is a planned and systematic set of procedures to document the various steps in a measurement process and to give confidence that the results of are of good quality. The need to generate confidence in the results requires that a quality assurance procedure be applied to data acquisition.

A proper detector efficiency calculation and several correction factors (matrix, coincidence correction, etc.) have to be taken into account when high accuracy and precision data have to be reported. Estimation of activity uncertainty and correction factors used in gamma-spectopmetry is important because this method is extensively used in environmental monitoring and research. The Monte Carlo method has been found to be a powerful tool for improving the accuracy and precision of gamma- spectrometric measurements of marine samples.

TABLE III. AN EXAMPLE OF THE UNCERTAINTY BUDGET COMPUTED FOR ^{60}Co IN MARINE SEDIMENT

PARAMETER	VALUE
Energy	1173.2 keV
Emission probability	0.99857 ± 0.00022
Half life	1926 ± 1 days
Detector efficiency	0.0415 ± 0.0008
Correction for decay in the ΔT time interval(K_1)	0.9543
Correction for decay during measurement (K_2)	0.9996
Self-attenuation correction factor (K_3)	0.959 ± 0.009
Correction for loss due to random summing (K_4)	0.999988
Coincidence correction factor (K_5)	0.84 ± 0.01
Correction factor for decay during the sampling period	1.0
Total area of the peak	1348
Total area of the background peak	592
Net area of the sample peak	1073 ± 39
Net area of the background peak	113 ± 30
Background corrected net area of sample peak	1019 ± 42
Specific Activity (Bq/kg)	2.3 ± 0.1

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MARINE OLIGOTROPHY AND ELEMENT BIOGEOCHEMISTRY

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Abstract

A biogeochemical model has been developed that explains the inverse and non-linear relationship between Po-210 concentration in zooplankton and their biomass, under oligotrophic conditions in French Polynesia. This study identified other elements with comparable accumulatory behaviours to Po-210 in phytoplankton, seston and zooplankton, that are proposed to be critical to its enhanced environmental levels under oligotrophy. Field investigation in the Gulf of Papua showed that four of these *a priori* identified elements *viz* Cd, Co, Pb and Mn, as well as Cr and Ni, showed elevated water concentrations with reduced biological productivity, results that are consistent with those previously obtained for Po-210 and the proposed explanatory model. These findings point to the enhanced susceptibility of oligotrophic systems to comtamination from particle-reactive elements.

1. INTRODUCTION

Previous studies have reported on elevated Po-210 levels in zooplankton from the oligotrophic marine systems of French Polynesia, although paradoxically the region is remote from continental sources of Po-210's progenitor, Rn-222. Zooplankton Po-210 concentrations were also shown to be inversely and non-linearly related to zooplankton biomass [1, 2]. These results indicated the enhancing effect of oligotrophy on the bioaccumulation in zooplankton of Po-210, the most significant radionuclide with respect to radiological dose to humans from their consumption of seafoods [3, 4]. A biogeochemical model developed *a priori* to explain this phenomenon focussed on the ability of zooplankton faecal pellets to remove particle-reactive Po-210 [5, 6] from the euphotic zone, at a rate that is dependent on zooplankton biomass. This model both simulated the inverse and non-linear shape of the empirical relationship between Po-210 concentration in zooplankton and their biomass, and also predicted Po-210 concentrations in zooplankton that were similar to the measured values [2]. In this study we investigated the proposed biogeochemical effect of oligotrophy on the enhancement of other elements in the marine euphotic zone.

2. MATERIALS AND METHODS

Two approaches were used to further study this effect of oligotrophy and our interpretation of it, as described above, *viz :*

i) identification of those attributes of the proposed biogeochemical model that are most important to an explanation of the enhancing effect of oligotrophy, (as reflected in reduced zooplankton biomass), on their Po-210 concentrations. These attributes of Po-210 are compared with those in a range of elements [7] to determine a) the relative uniqueness of Po-210 and b) other elements most likely to be enhanced in their water concentrations under oligotrophy, and consequently accumulated to greater degree by zooplankton; and

ii) an empirical investigation of the water concentrations of six trace metals (Cd, Co, Cr, Ni, Pb and Mn) as a function of biological productivity in the Gulf of Papua.

3. RESULTS

3.1 Model structure

In Fig. 1 is shown a diagram and brief summary explanation of the conceptual model developed to explain the inverse relationship between Po-210 concentrations in zooplankton and their biomass in the oligotrophic French Polynesian waters, as detailed in Jeffree et al.[2]. By the following chain of causation a reduction in the biomass of zooplankton can lead to increases in their Po-210 concentration: *reduced zooplankton biomass → reduced rate of faecal pellet production → reduced rate of Po-210 removal from the euphotic zone → enhanced Po-210 concentrations in the water of the euphotic zone → enhanced Po-210 concentrations in enviromental compartments, including zooplankton.*

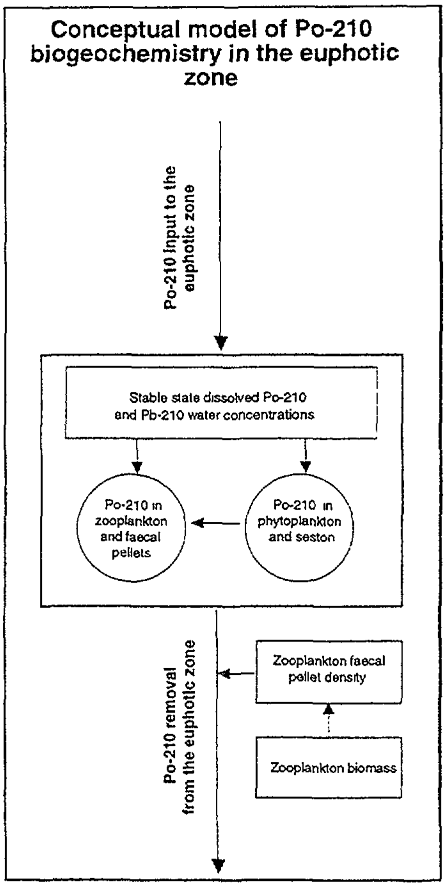

FIG. 1. (a) Po-210 input to the euphotic zone results from Rn-222 emanating from the continental regions, its subsequent decay to Pb-210 which enters the sea surface and decays to produce Po-210, (b) Po-210 is removed from the euphotic zone predominantly through its association with phytoplankton and seston and subsequent incorporation into the faecal excreta of zooplankton, that rapidly depart the euphotic zone, (c) phytoplankton and seston reflect Po-210 (dissolved) concentration in water. The main uptake route of Po-210 by zooplankton will probably be via ingestion of these micro-particles, but can also occur through direct uptake from water. The steady-state Po-210 concentration in the euphotic zone therefore indirectly determines the stable-state Po-210 level in its ambient zooplankton, according to its concentration factor [7].

Element-specific aspects of the model are i) concentration factors (CFs) for Po-210 in phytoplankton and zooplankton, ii) its Kd for seston, and iii) its continual input to the euphotic zone. Moreover it shows general unidirectional movement through the euphotic zone in the thermally stratified water column typical of marine oligotrophic systems [8].

From the model structure it follows that; i) a higher CF for an element in faecal pellets would lead to its enhanced rate of removal from the euphotic zone; therefore reduced zooplankton density would lead to its enhanced steady state water concentration in the euphotic zone, ii) the combination of high CFs of an element in all three- phytoplankton, seston and zooplankton- would enhance the effect of oligotrophy on element concentrations in water and zooplankton. Also an element's concentration in faecal pellets is related to its CF in phytoplankton and seston Kd, of which the faecal pellets are composed.

To determine the degree to which Po-210 is concentrated, relative to other elements, percentage distributions for 59 elements were generated for their CFs [log10(n+1)] in zooplankton and phytoplanton, and Kd (pelagic) [log10(n+1)] for seston. Table 1 shows a correlation matrix for these three sets of values, with positive and highly significant ($P<0.001$) relationships between each of them. These results indicate the similarity in the accumulatory behaviour between phytoplankton, zooplankton and seston among these elements, that is not restricted to only Po-210.

TABLE I. CORRELATION MATRIX OF CONCENTRATION FACTORS (CFs)+ IN PHYTOPLANKTON AND ZOOPLANKTON AND SESTON Kds (PELAGIC) VALUES+, BASED ON 59 ELEMENTS*.

	Phytoplankton	Zooplankton
Kds	0.75	0.67
Phytoplankton	-	0.86

+ [log10(n+10], * using IAEA recommended values [7].

The following selection strategy was used to identify elements similar to Po-210. Those elements that fell within the range extending from one order of magnitude less in concentration (CF and Kd) than the recommended value for Po-210 [7] and all those above, were selected. The following percentages of elements were found for each group: zooplankton-27%; phytoplankton-56%; and seston-20%. Among these elements, those that also occur in all three (underlined), or 2 out of three of phytoplankton, seston and zooplankton were: Sc, Mn, C, Fe, Co, Zn, Se, Zr, Ru, Ag, Cd, Sn, Ce, Eu, Gd, Dy, Ir, Hg, Pb, Ac, Th, Am, Cm, Bk, and Cf. According to the proposed model these elements would be more likely to show enhanced environmental concentrations with declining productivity, under general oligotrophic conditions.

3.2 Empirical study

Among several particle-reactive trace elements measured in the oligotrophic region of the Gulf of Papua [9] Cd, Co, Mn and Pb would be expected to show the enhancing effect of oligotrophy on their water concentration, according to our model, for the following reasons; i) their relatively constant input rate to the euphotic zone [10], ii) all have established physiological uptake mechanisms and/or are associated with biogenic particles in the water column [11, 12], and iii) similar Cf and Kds values to those for Po-210, as identified according to the selection strategy outlined above [7].

In Fig.2a dissolved water concentration for Cd, Co and Mn are plotted as a function of the particle removal rate Ψ, deduced from Th-234/U-234 activity ratios, a surrogate measure of biological productivity [13, 14]. The inverse and non-linear relationship is evident, and similar to that previously shown for Po-210 [2]. Fig. 2b shows the water concentrations of three other trace elements (Cr, Ni, Pb), also plotted against the particle removal rate. In the case of these latter elements, although an increase in water column concentrations is associated with reduced particle removal rates, or biological activity, the effect of oligotrophy is not as non-linear.

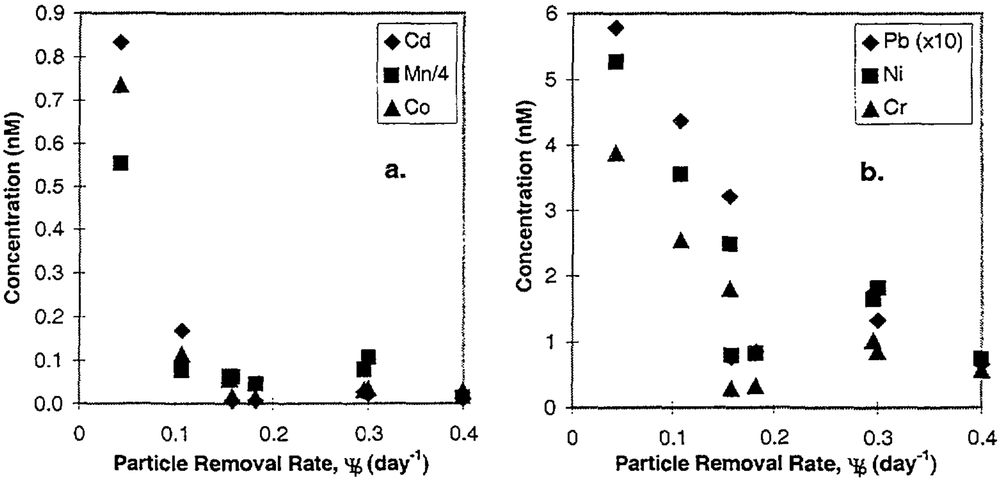

FIG. 2 Concentration vs. particle removal rate

4. DISCUSSION

This study identified a set of elements that have accumulatory capacities in phytoplankton, seston and zooplankton that are comparable to those of Po-210, based on a consensual collection of empirically-based data [7]. This set represented a relatively high percentage (>40%) of all the elements (59-60) that were investigated. According to the proposed biogeochemical model (Fig. 1) such elements are predicted to show enhanced concentrations in the water and resident zooplankton with declining productivity, within generally oligotrophic marine environments. Empirical evaluation of a subset of the element set, undertaken with water concentrations of Cd, Co, Cr, Mn, Ni and Pb measured in oligotrophic environments that varied over an order of magnitude in their biological productivity, showed elevated levels as biological productivity declined (Fig. 2). The degree of non-linearity observed in the relationships between biological activity and the dissolved water column concentrations of three of these elements (Cd, Co, Mn) were very similar to that displayed by Po-210 [2]. Increased water column concentrations of the elements Cr, Ni and Pb were also observed under oligotrophic conditions, however a lesser degree of conformity was evident with the empirical results for Po-210 and associated mathematical model [2]. The difference between the observed behaviour of these two groups of elements may be due to physiological uptake and biological removal of Cd, Co and Mn, as well as physico-chemically induced association with settling particles. These results are therefore consistent with the proposed biogeochemical model and the predictions derived from it. Moreover, the results for those two elements that were not included in the initial study set (Cr and Ni) also showed a pattern of enhanced water concentration with declining productivity, suggesting that the selection strategy employed for elements comparable to Po-210 may have been too rigorous.

With regard to the specific mechanism(s) underpinning the inverse relationship between Po-210 in zooplankton and their biomass, a model, including an equation form with a first-order loss exponent, was used to represent loss of Po-210 from the euphotic zone, at a rate that is dependent on zooplankton biomass and its associated faecal pellet production rate. This equation simulated the inverse empirical relationship, that is comparable to those seen in this study (Fig. 2) for other elemental water concentrations as a function of biological productivity. The shape of the modelled relationship was simply an outcome of the mathematical behaviour of the equation form, that was chosen *a priori* to represent the underlying biogeochemical process [2]. Site-specific empirical parameter values were not available for fitting to the model, however the most appropriate available values did generate values within a factor of 5 of closer to the empirical Po-210 concentrations in zooplankton. Such a result is generally supportive of the model. However, given the eclectic nature of the empirical parameter values used, such results cannot preclude the operation of another mechanism such as the regeneration of trace elements [11] that is enhanced with increasing oligotrophy [15]. But such an exclusive interpretation based on regeneration would require its operation in an exponential fashion for Po-210 and other elements, with declining productivity in oligotrophic environments.

These results are also relevant to the following environmental issues;

- oligotrophic marine systems, that represent about 50% of the world's oceans [16] are likely to be more susceptible to contamination by particle-reactive elements, compared to more productive systems, and
- the geographical extent and intensity of greenhouse-related oligotrophy may be increased in the future due to elevations in surface water temperatures and enhanced thermal stratification of the water column.

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THE USE OF NATURAL ^{14}C AS A TRACER TO IDENTIFY THE INCORPORATION OF YOUNGER MATERIAL INTO THE ORGANIC COMPONENT OF SEDIMENTS FROM THE CARPENTARIA BASIN, AUSTRALIA

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Abstract

A "chemically inert" organic fraction was isolated from samples taken from a sediment core that was collected from the Gulf of Carpentaria, lying between Australia and Papua New Guinea. Accelerator mass spectrometry (AMS) ^{14}C ages obtained from this fraction become younger with depth, the maximum ^{14}C concentration being 107% M, then become older again. The shape of the plot of apparent ^{14}C age with depth can be compared to a typical concentration plot of a compound being passed through a chromatographic column. The shape of the so-called natural chromatogram has a relatively sharp leading edge, then gradually tails off. Stable carbon isotope values indicate that the material is most probably a non polar compound (or mixture) of yet unknown origin.

1. INTRODUCTION

The Gulf of Carpentaria is a large, shallow (<70m) epicontinental sea lying between Australia and Papua New Guinea. It is connected to the Arafura Sea to the west across a 53m sill located below sea level, and to the Coral Sea to the east across the 12m deep Torres Strait (see Fig 1B). During a large part of the Quaternary period (viz. the last 2 million years of the geological record), the Gulf was disconnected from the ocean, and a large lake was formed periodically in this large depression. The lake, when it last existed prior to the last sea-level transgression that commenced after the Last Glacial Maximum (= LGM) ca. 20 cal ka and that culminated in its flooding by marine waters at approximately 9 cal ka, may have had a surface area of some 150,000 km^2. The existence of this lake had been predicted by Nix and Kalma [1] based on Phipps' [2] early bathometric reconstructions for the Gulf. Torgersen [3] conducted an extensive marine cruise in the Gulf in 1982, and this resulted in the collection of some 35 gravity cores with good seismic control. Most cores were taken below 60m of water depth. Investigations in the Gulf that followed the cruise are presented in [3] and [4], and references therein. When full around the time of the LGM, "Lake Carpentaria" (see Fig. 1B) retained fresh to slightly saline water and was less than 10 m deep; for more information, refer to [4-6]. Torgersen et al., [4] have summarised the stratigraphic units recovered in the

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cores and have provided a ^{14}C chronology for the top 220 cm of the most representative core GC-2. The stratigraphic section has been divided into 5 units which are recognised in most cores. These units are schematised graphically in Fig. 1C.

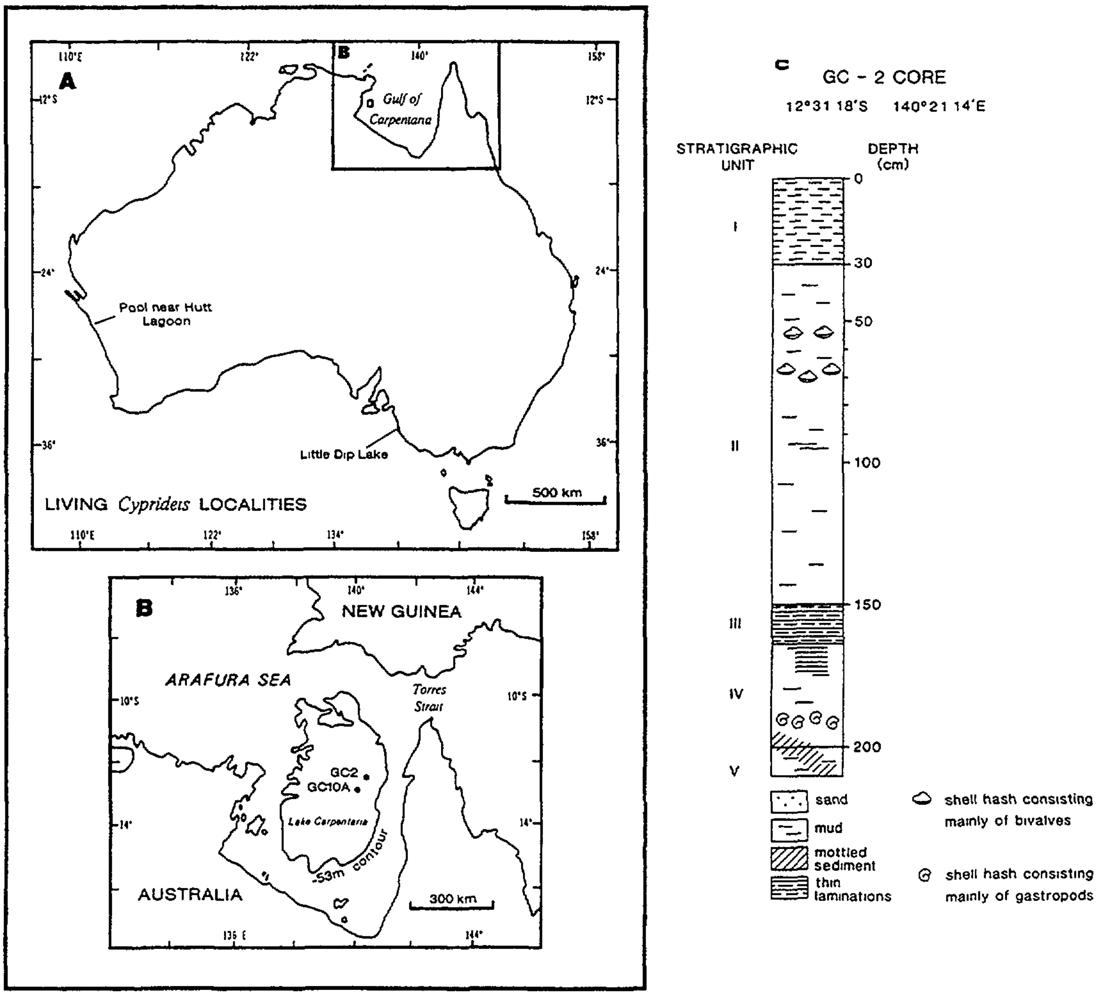

FIG. 1. A. Location map showing the Gulf of Carpentaria positioned between Australia and Papua New Guinea. ***B.*** *is a more detailed map showing the extent of "Lake Carpentaria" during periods of low sea levels, as well as the position of core GC-2 which is located more than 60 km from the present-day coastline of the Gulf.* ***C.*** *is a simplified stratigraphic section of core GC-2 showing the five principal lithological Units (I-V) discussed in the text.*

The top unit I (0-30 cm) consists of grey-green, siliciclastic to bioclastic sediments which contain abundant marine molluscs (including pteropods), bryozoans, ostracods and foraminifers. This unit was deposited under truly marine conditions, but it contains some reworked faunal elements from the previous underlying units (for further details, refer to ref 5). It is very likely that the sediments representing the present-day deposition at the bottom of the Gulf are missing from the core as the gravity coring technique frequently compresses or loosens the often 'soupy' layers at the bottom of lakes or the oceans. Unit II consists of firm dark grey siliciclastic sediments containing ostracods and foraminifers deposited under lacustrine conditions. It is the thickest unit in core GC-2 and extends down to 150 cm. Radiocarbon ages give the time of deposition for this unit between 9 and 25 cal ka .

Unit III is characterised by fine laminations with layers consisting of small calcite crystals (10-20 μm long) alternating with siliciclastic sediments. This unit was deposited in a stratified lake, and this is further confirmed by evidence of bleaching and partial dissolution of biogenic carbonates such as ostracods and foraminifers and the presence of pyrite crystals indicative of dysaeorobic conditions. This unit in core GC-2 was deposited between 25 and 30.5 cal ka.

The underlying Unit IV consists of shelly siliciclastic sediments with abundant molluscs, ostracods and foraminifers. Some horizons in this Unit are best described as consisting of a shell hash. Postulated conditions [ref. 5] for this Unit are those of a very productive freshwater lake during the 30.5- 41.9 cal ka period. Dates for this Unit have been extrapolated through core GC-10A which contains the best representation of this Unit. The bottom of the core is characterised by mottled, siliciclastic sediments that have undergone some pedogenesis/aerial exposure; this is typically Unit V which contains reworked marine faunas mixed with some freshwater/low salinity ones, and for which an age >41 cal ka is postulated. All the dates referred to for this section were measured on bulk carbonates [see ref 4].

The purpose of this study has been to compare ^{14}C ages of "chemically inert" organic carbon recovered from core GC-2 with those of foraminifera and ostracods (biogenic carbonates) from the same core collected at regular intervals, using the technique of accelerator mass spectrometry, with the aim of determining the best possible material for dating sedimentary sequences formed under a marginal environment which registers marine/non-marine transitional facies.

2. METHODS

CO_2 from each foram or ostracod sample was obtained by the standard acid evolution technique using dry HP_3O_4. For organic extractions, each sediment sample was subjected to a series of three solvent extractions using solvents of different polarity, in an ultrasonic bath. A full explanation of the procedure has been given previously [6]. From the lack of colour in the solutions, it was assumed that very little material was extracted from the organic component of the sediment samples. The samples were then treated with hot 2% NaOH solution, and it was found that the NaOH solutions remained only slightly coloured, indicating that there was very little NaOH soluble material in the sediment. The NaOH liquor was then separated by filtration, and the residue was treated with hot 10% HCl, rinsed and dried. CO_2 was obtained from portion of the NaOH insoluble component of each sample using the standard sealed tube technique with CuO. The procedure used for preparation of sample graphite for ^{14}C AMS determinations is as described by Fifield et al., [7]. The AMS determinations were carried out at the ANTARES AMS Facility at the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, NSW. Stable isotope determinations were carried out on portion of the CO_2 samples prepared for AMS graphite target preparation. The samples were analysed using a Europa Scientific 20-20 mass spectrometer.

3. RESULTS

Figure 2 indicates a plot of organic and inorganic paired ^{14}C ages using the AMS technique and facility at ANSTO. It shows that the inorganic carbon results form a reasonable sequence with depth, but the organic fraction ages actually become younger with depth down to 136 cm (107% M), then become older again. The shape of the organic age plot with depth can be compared with a typical concentration plot of a compound moving through a chromatographic column, having a relatively sharp leading edge and a long tail. From this observation there is a strong possibility that young (post atmospheric nuclear testing) non-polar organic material is moving down the profile in a similar manner to a chemical compound moving through a chromatographic column. At this stage no analytical work has been carried out to identify the contaminant. Table 1 lists $\delta^{13}C$ values (with respect to the PDB standard) of the organic fractions with ^{14}C ages.

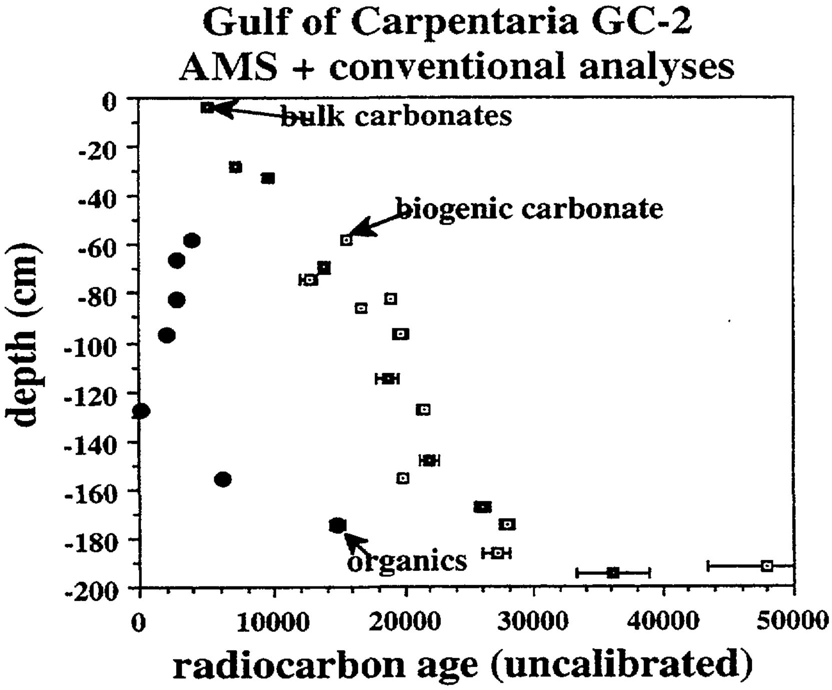

FIG. 2. Plot of all the organic as well as inorganic paired ^{14}C results for all the samples prepared and analysed for AMS.

TABLE I. $\delta^{13}C$ VALUES AND ^{14}C AGES OF ORGANIC FRACTIONS FROM LAKE CARPENTARIA.

ANSTO No.	Submitter's Code	$\delta^{13}C$ (‰)	^{14}C Age
OZB 203	GC2 57-58	-17.29 ± 0.2	4020 ± 80
OZB 202	GC2 66-67	-13.39 ± 0.2	2820 ± 70
OZB 204	GC2 82-83	-11.69 ± 0.2	2790 ± 50
OZB 205	GC2 96-97	-13.22 ± 0.2	1980 ± 40
OZB 322	GC2 127-128	-15.98 ± 0.2	107.0 ± 1.0
OZB 201	GC2 155-156	-15.79 ± 0.2	6150 ± 60
OZB 199	GC2 174-175	-20.83 ± 0.2	14,800 ± 530

At this stage, given that each fraction consists of a young component plus a much older, possibly original component, there seems to be no apparent pattern in the results. However, the $\delta^{13}C$ value for the youngest fraction (OZB 322, -15.98 ± 0.2‰) quite possibly indicates that the younger material is marine in origin.

4. CONCLUSIONS

The identification of this material as a contaminant is extremely significant in that one can actually observe the material moving down the sedimentary profile as if it were a chromatographic column. It appears that the reversal to older material at around 127-128cm depth corresponds to the change in lithology in core GC 2, at unit III,which consists of finely laminated sediments. It may be that the nature of the sediments in unit III causes this unit to act as a somewhat impervious barrier to the younger organic signal travelling down the sedimentary column. This organic "contaminant" may be a result of anthropogenic pollution or it may be the result of a natural phenomenon. It gives every indication of being a single event. Stable isotope determinations do not indicate a specific pattern of mixing of the organic material. Further work will be carried out in order to examine the extraction techniques used so that more efficient separations can be achieved. Categorisation of the younger organic component will also be carried out in order to pinpoint the origin of the material. The ^{14}C activity of the youngest sample measured indicates a probable age within the mid 60's. The significance of these results with respect to future studies of marine and lake sediments lies in the way in which the organic component moves down the profile and its relationship with sediment type.

Acknowledgements

Patrick De Deckker and John Head acknowledge an Australian Research Council Grant which helped defray some of the costs involved in this work. Allison Barrie carried out the sample preparations for AMS targets under J. H.'s supervision; she also diligently and painstakingly picked the microfossils from the various horizons of core GC-2. The core was oroginally obtained by T. Torgersen through an MST grant.

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WORLD-WIDE REDISTRIBUTION OF ^{129}IODINE FROM NUCLEAR FUEL REPROCESSING FACILITIES: RESULTS FROM METEORIC, RIVER, AND SEAWATER TRACER STUDIES

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Abstract

Releases of the long-lived radioisotope of iodine, ^{129}I, from commercial nuclear fuel reprocessing facilities in England and France have surpassed natural, and even bomb test inventories. ^{129}I/^{127}I ratios measured in a variety of environmental matrices from Europe, North America and the southern hemisphere show the influence of fuel reprocessing-derived ^{129}I, which is transported globally via the atmosphere. Transport and cycling of I and ^{129}I in the hydrosphere and in soils are described based on a spatial survey of ^{129}I in freshwater.

1. INTRODUCTION

The database for iodine (^{127}I) and the ratio of ^{129}I/^{127}I in natural materials is relatively small, and highly scattered, owing to inherent variability for different rock and water types, and to difficulties in the measurement of both the concentration and isotope ratio. Iodine concentrations in surface waters are quite low in general, and measurement of ^{129}I/^{127}I ratios in iodine from natural materials is by accelerator mass spectrometry, available at only a few laboratories worldwide. We made a spatial survey of ^{129}I/^{127}I ratios and stable iodine concentrations in freshwater and seawater, in order to determine sources of ^{129}I.

Given the geochemical behavior of iodine, which is generally conservative as an anion, but has an affinity for organic material; and the steep increase of ^{129}I due to fuel reprocessing emissions, ^{129}I is a good candidate for a hydrologic and biogeochemical tracer on a global scale. The long-lived isotope of iodine, ^{129}I (half-life 15.6 m.y.), is produced naturally in the atmosphere by the interaction of high-energy cosmic rays with xenon isotopes. Beginning in about 1945, and peaking in 1963, nuclear bomb tests added tens of kilograms of ^{129}I to the atmosphere, resulting in ^{129}I/^{127}I ratios several orders of magnitude higher than natural ratios [1, 2]. Unlike most radionuclides produced during atmospheric bomb testing which have returned to near pre-nuclear levels, the amount of ^{129}I in the atmosphere and in surface waters has continued to increase due to releases from nuclear fuel reprocessing facilities. ^{129}Iodine releases into the North Sea from two such fuel reprocessing facilities (at Sellafield, England and Cap de La Hague, France) continue at very high levels [3], providing in effect, a point source for the total surface inventory.

The total natural ^{129}Iodine in the surface environment was about 80 kg ($5x10^{-4}$ kg in the atmosphere). For comparison, atmospheric bomb tests produced 45 kg [3], and the Chernobyl reactor accident released 1.3 kg [1]. On a larger scale, the facilities at Sellafield and La Hague have cumulatively released 1440 kg since operations began in the late sixties [3]. As of 1994, direct ^{129}I releases from the facilities at Sellafield and LaHague into the ocean were about 200 kg/yr, with a steep increase from the LaHague facility from about 1990 and continuing to the present [3]. Iodine is a volatile, atmophile element. McKay et al. [4] give evidence that the method of trapping off gases at the Sellafield facility allows 3-6% of the ^{129}I produced to be released in gaseous discharges. If conditions were similar at the

Cap de LaHague facility, that would indicate total releases of 6-12 kg/yr to the atmosphere from both facilities combined. Another estimate based on measurements of iodine activity in the air near the Sellafield plant, puts this figure at 9% (or 18 kg/yr; [5]).

Releases of ^{129}I to the atmosphere allow for long-range transport, given the relatively long residence time of iodine in the atmosphere, and its high degree of reactivity. The ^{129}I transported atmospherically is deposited on the continents by (mainly wet) deposition, where it infiltrates soil, is taken up by plants, and is washed into rivers and other surface water bodies. Potential applications of ^{129}I as a tracer include: dating recently recharged groundwater, tracing sources of salt in river watersheds, tracing and dating post-nuclear terrestrial organic material in the nearshore marine environment, tracing atmospheric transport and deposition of iodine, and defining the spatial extent of the influence of fuel reprocessingemissions.

2. METHODOLOGY

A thorough description of the method of extrraction of I from water samples can be found in Ref. [6]. Iodine concentrations in raw water samples and in extracts were measured by inductively coupled plasma mass spectrometry or by ion chromatography. ^{129}I/^{127}I ratios were measured by AMS at Purdue University's PRIME Lab. Procedures for running ^{129}I are described in Ref. [7]. Because the ratios measured for water samples were all > 5.0×10^{-12} (well above the detection limit of 5×10^{-15}), errors due to counting statistics in the detector are relatively small, and 1 sigma errors are <10%. Procedural blanks are .07-0.5×10^{-12}, which were in the range expected for the carrier iodine, and therefore no corrections to the measured ratios were made for blanks.

3. RESULTS AND DISCUSSION

Stable iodine concentrations and ^{129}I/^{127}I ratios are shown graphically in Figs 1-3. In all locations and in all matrices examined, there is evidence for ^{129}I levels in excess of what is expected from bomb fallout alone. This is most evident in meteoric water samples, where relatively rapid cycling takes place, and where there is relatively little dilution by stable iodine.

The ^{129}I that is released directly into the atmosphere from the fuel reprocessing facilities clearly is not distributed evenly over the globe. ^{129}I/^{127}I ratios measured in epiphytes within 60 km of the Sellafield site were 15 to 6693×10^{-8} [8], two to four orders of magnitude higher than ratios measured in Germany and other parts of Europe [9]. Our ratio for meteoric water from Sauverny, France (near Geneva, Switzerland) is the highest in Fig. 1, and is more than an order of magnitude greater than all but two samples measured in the U.S. In order to estimate the amount of fuel-reprocessed ^{129}I potentially distributed great distances from the fuel reprocessing facilities in Europe, we calculate the "standing crop" of ^{129}I in the atmosphere over the continental U.S., and extrapolate to the northern hemisphere. A conservative estimate of the residence time of total iodine in the atmosphere is 14 days [10]. Using a global precipitation rate of 4.96×10^{17} kg/yr and our median stable iodine concentration in rain of 1.7 ng/ml, one calculates a flux of iodine from the atmosphere of 8.4×10^{8} kg/yr. The median ^{129}I/^{127}I ratio measured in rainwater for U.S. locations is approximately 2100×10^{-12}. Here it is important to note that 80% of atmospheric radioiodine deposition (at mid-latitudes with about 1 m/yr of rainfall) occurs during precipitation events; 20% by dry deposition [11]. Assuming no inter-hemispheric mixing, and using the median ratio, mass of ^{127}I in the atmosphere, and 14 day residence time, the mass of ^{129}I in the atmosphere at any given time is 0.04 kg. The roughly calculated 0.04 kg can be compared with 0.7 kg (again using the 14 day mean residence time) of the estimated 18 kg/yr released from Sellafield and LaHague in the atmosphere at any given time. Given the great distance between the source and the continental U.S., the fact that approximately 6% of the estimated atmospheric releases reaches the sampling area seems reasonable.

As fine aerosols or in gaseous forms, ^{129}I can be mixed from top to bottom of the troposphere very quickly (< 1day). Global tropospheric circulation patterns are such that in winter months, the air mass over northern Europe is transported by strong winds in an easterly-north-easterly direction. However, during summer months, there is a significant wind component that drives the air mass to the south, along the western edge of Africa, and across the Atlantic via the trade winds. Both of these

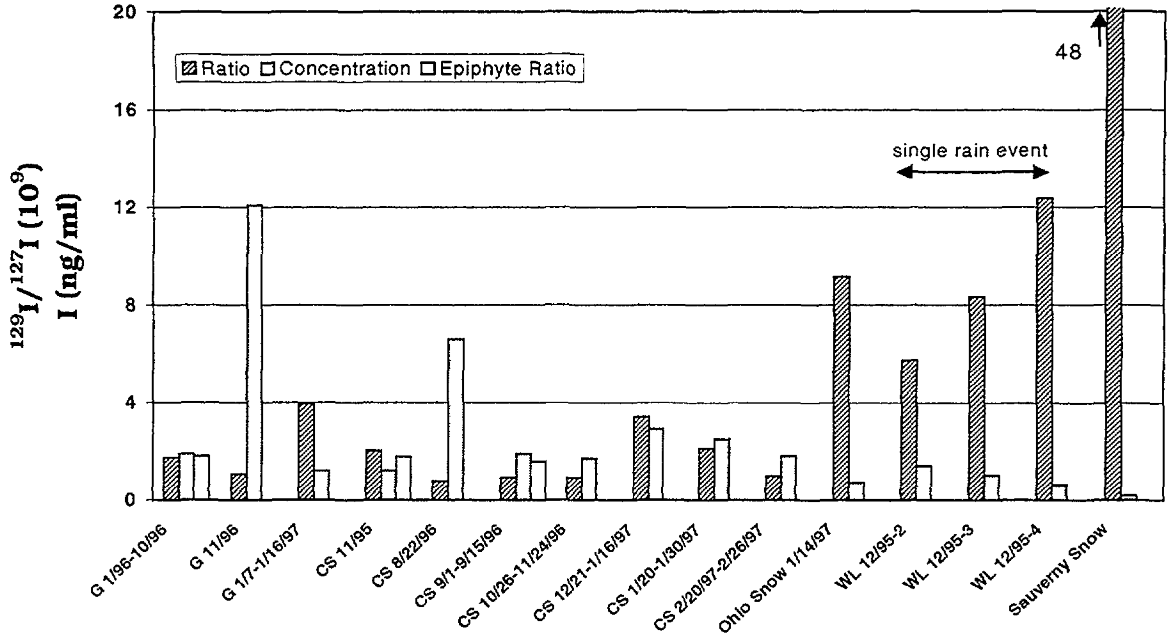

FIG. 1. Meteoric water and selected epiphyte iodine concentrations and ^{129}I/^{127}I *ratios [6]. Sample locations, on x axis, are arranged from coastal locations (left) to inland (right). Sample locations are: G-Galveston, Texas; CS-College Station, Texas; Mansfield, Ohio; WL-West Lafayette, Indiana; Sauverny, France.*

circulation patterns could result in transport of ^{129}I from European fuel reprocessing facilities to the continental US.

3.1 Rivers

^{129}I/^{127}I ratios measured in river waters range over 4 orders of magnitude, from 76x10^{-12} to 850,000x10^{-12}. Immediately obvious are rivers with point sources for ^{129}I in their watersheds (Fig. 2). These include the Savannah River, with the Savannah River Plant upstream from the sampling location, and the Columbia River, with the Hanford Facility upstream of the sampling site. Several studies have shown that these sites have had purposeful and accidental releases [12, 13] of radionuclides, including ^{129}I. Interestingly, two rivers near those directly affected by point source runoff are indirectly affected, most likely by atmospheric releases. The Altamaha River, in northern Georgia does not drain the Savannah River Plant area but still has a greatly elevated ^{129}I/^{127}I ratio. Likewise, the Hood River, a tributary to the Columbia, downstream from Hanford, has a ratio much higher than rivers of similar iodine concentration. In these two cases, historical releases of ^{129}I to the atmosphere [12, 13] have resulted in elevated levels of ^{129}I in watershed soils and plants, and this ^{129}I has been subsequently transported to the rivers during runoff.

We attribute the high ratios and ^{129}I concentrations observed in two European rivers (i.e., the Rhone and Rhine Rivers) to the proximity of the main source for ^{129}I, *viz.* the nuclear fuel reprocessing facilities at Sellafield, England and at Cap de la Hague, France. These elevated levels must likewise be due to atmospheric emissions and rainout followed by runoff, since liquid releases go directly to the English Channel. The ratio measured in the Rhine River is somewhat lower than the ratio measured in the snow from France, while the Rhone River had a much higher ratio. These variations are likely due to spatial variations in atmospheric re-distribution and fallout of fuel reprocessing ^{129}I.

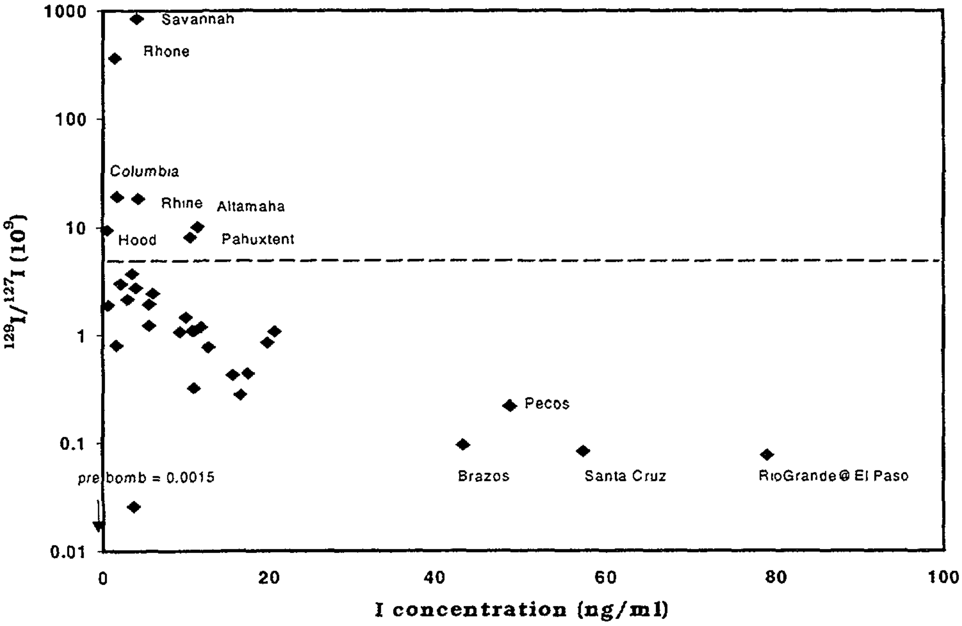

FIG. 2 Results from a spatial survey of (mainly North American) rivers. Rivers with point sources in their watershed (above dotted line) have greatly elevated ratios compared to those affected

All $^{129}I/^{127}I$ ratios and ^{129}I concentrations observed in other rivers, i.e., those outside the range of influence of point sources are still elevated above levels attributable solely to bomb fallout. Consider for example, for the Mississippi River watershed, with a drainage area of 3.27×10^{12} m^2. Using a cumulative bomb fallout of 7.5×10^{11} atoms $^{129}I/m^2$ [14] and a residence time of iodine in soil of 100 yr [12, 15], one calculates a flux of 2.5×10^{22} atoms/yr into the Mississippi River from watershed soils. The measured river concentration of 8×10^7 atoms/kg and flow rate of 5.8×10^{14} kg/yr, provides a flux nearly twice as high, 4.6×10^{22} atoms/yr. Addition of older, lower ratio iodine from watershed soils tends to reduce ratios in river water below those found in rainwater.

Figure 3 is a mixing diagram for rivers other than those affected by local sources, as discussed above. A two component mixing trend is evident. End members are an atmospheric component, with a broad range of values, and a soil leachate component with a high iodine concentration and pre-bomb ratio (1.5×10^{-12}; [16]). The atmospheric component varies considerably, due to unevenness in the rainout. Stable iodine concentration in rain depends (weakly) on distance from the coast, and on the chemical form of the iodine. ^{129}I and ^{127}I are not well mixed in the atmosphere, nor should we expect them to be given their disparate sources. Accordingly, in rivers which plot within and near the atmospheric end member oval, meteoric (oceanic) cyclic salt provides the main source of iodine, and atmospheric emissions from nuclear fuel reprocessing represent the main source of ^{129}I. The Connecticut, Yukon, MacKenzie, and Potomac Rivers are among this type of river. While these rivers have been categorized as having a larger component of cyclic salt than the average world river [17], for most constituents they are still rock-dominated. Because iodine is relatively much less abundant in rock-forming minerals, the cyclic salt component of iodine assumes greater significance.

Rivers with high iodine contents (e.g., the Rio Grande, the Pecos, and to a lesser extent the Mississippi and southeastern USA rivers) show some affect by anthropogenic ^{129}I in their iodine isotope ratios, but show a component of pre-anthropogenic ^{129}I. The rivers with the highest I concentrations have watersheds in arid regions where and water use is very high. Over the past several decades, the salt

content of these rivers has increased dramatically, mainly due to non-point source runoff and return flow from cultivated fields. In these agricultural areas, high evapo-transpiration and inefficient irrigation techniques combine to disturb the natural salt balance in soils. In addition, contributions of iodine from fertilizers, herbicides, pesticides, and from certain crops, which may concentrate iodine, should also be considered [18]. Because pre and post-bomb atmospheric $^{129}I/^{127}I$ ratios differ by 3 orders of magnitude, addition of a small fraction of anthropogenic iodine can raise the measured ratio substantially.

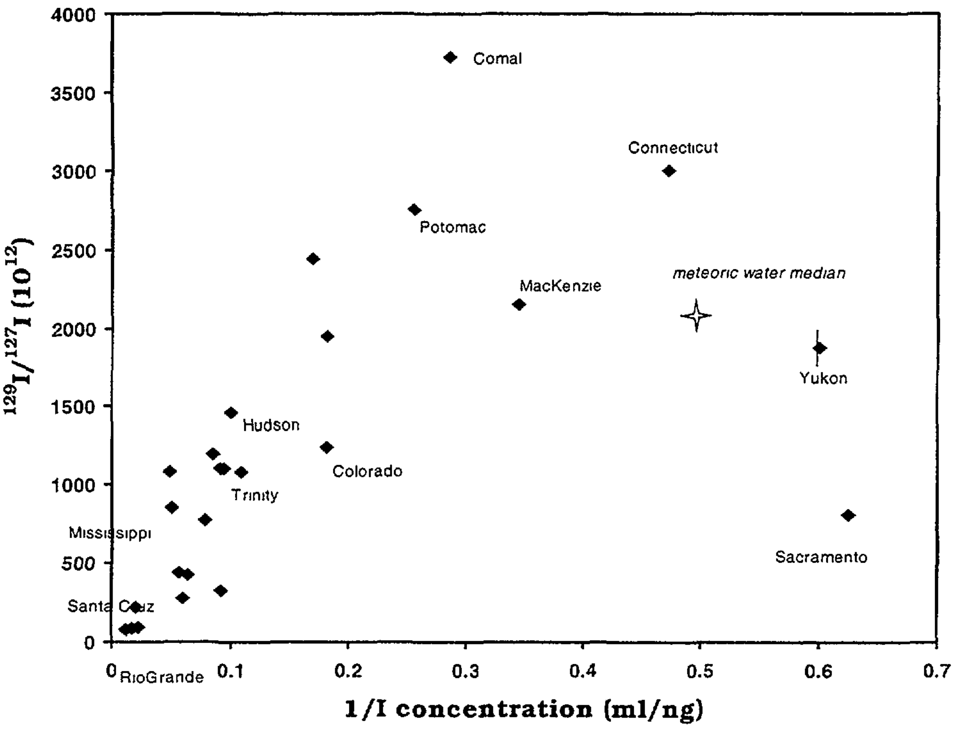

FIG. 3. Mixing diagram for rivers not affected by local point sources for ^{129}I. Possible mixing between atmospheric and soil-derived endmembers is evident. A representative 1σ error bar is shown (Yukon).

3.2 Comparison with seawater

The high ratios observed in rivers indicate a significant worldwide flux of ^{129}I off the continents into the oceans; about 0.5 kg/yr. However, 30 years accumulation of this flux, all in the ocean's mixed layer (top 100m), would result in a seawater ratio of 5×10^{-12}; much lower than that observed. Measurements of $^{129}I/^{127}I$ ratios in seawater in areas distant from Sellafield and La Hague include those by Santschi et al. [19] in the mid-Atlantic Bight, and Schink et al. [20] in the Gulf of Mexico. Ratios near the surface are 107×10^{-12} and 67×10^{-12}, respectively. Another profile from the Gulf of Mexico taken in 1996, but prepared by the method of chemical extraction described above, gave similar results, with a maximum ratio of 95×10^{-12}. While these ratios are about an order of magnitude lower than those observed in most rivers from the adjacent continent, they are not influenced by runoff from the continent. Current-born transport of fuel reprocessing ^{129}I from the North Sea comprises the majority of the ^{129}I measured in seawater even in locations remote from the source.

3.3 ^{129}I in the Southern Hemisphere

Almost all nuclear activities are restricted to the northern hemisphere: all declared and threshold nuclear powers, the entire reprocessing capacity and more than 99% of the nuclear power production are located in the northern hemisphere. Investigation of the presence of ^{129}I in the Southern Hemisphere is thus a good test for the global transport of this isotope. We are in the process of collecting a representative set of samples from the southern continents, but have data so far from lakes in Australia and New Zealand. The ^{129}I concentrations found for Australia and New Zealand are quite similar, from 5×10^5 to 5×10^7, with the New Zealand values at the lower end of this range. Although the database is still very limited, these observations suggest that ^{129}I concentrations are in general lower by one order magnitude than in the northern hemisphere (but still significantly above pre-bomb levels) and that ^{129}I concentrations and $^{129}I/^{127}I$ ratios are above the levels expected for fallout from atmospheric testing.

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CARBON ISOTOPES IN SOM, POM AND DOM FROM DUTCH COASTAL WATERS AND ESTUARIES

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Abstract

Results of analyses of carbon isotopes in Sediment Organic Matter (SOM), Particulate Organic Matter (POM) and Dissolved Organic Matter (DOM) in coastal waters and estuaries are discussed.

1. INTRODUCTION

Organic matter (OM) in marine sediments is a major carbon pool and of great importance for the global carbon cycle. Burial in coastal seas is high and buried organic matter can originate from either terrestrial or marine sources. To determine the origins of this organic matter stable carbon isotope ratios are often used as an indicator for the ratio between terrigenous and marine organic matter. In general a difference exists in the stable carbon isotope ratios ($\delta^{13}C$)[1] of marine phytoplankton and terrestrial organic matter. Marine phytoplankton has an average $\delta^{13}C$ value of –21‰ while terrestrial organic matter derived from so called C-4 plants, the major plant type in moderate climate zones, has an average $\delta^{13}C$ value of –27‰[1]. Using this difference an estimation of the ratio between terrestrial and marine organic matter can be made.

However, these values can vary considerably and the $\delta^{13}C$ values can change during diagenesis. The $\delta^{13}C$ value of marine phytoplankton depends on temperature and light [2]. Growth speed can also influence the $\delta^{13}C$ value. In a bloom the concentration phytoplankton is so high that the $\delta^{13}C$ of the carbon source, the dissolved inorganic carbon (DIC), can change due to isotopic fractionation by the phytoplankton.

There is also a wide variation in $\delta^{13}C$ values of various compounds in phytoplankton and other organisms. Carbohydrates and proteins have higher $\delta^{13}C$ values than lipids, on average a difference of 5l [3]. Carbohydrates and proteins are more labile than lipids and lipidic macromolecules like algaenans and cutans. Thus, by selective degradation of these labile compounds the $\delta^{13}C$ of the bulk can change considerably.

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[1] $\delta^{13}C$ is reported in permil vs. V-PDB.

^{14}a is the fractionation corrected relative ^{14}C abundance in pMC

Radiocarbon analysis of Particulate Organic Matter (POM) can be used to distinguish between fresh and old OM from erosion. In a marine system fresh OM is mainly produced by phytoplankton. POM transported by rivers to the sea appears to be derived only for a minor part of authochthonous phytoplankton and mainly from eroded soil or peat [1] and therefore has a higher age. An other source of old POM can be erosion of old deposits on the seafloor. Wang et al. [4] proposed adsorption of old dissolved organic matter to particulate matter in the deep ocean as a source of an old component in POM.

2. CHEMICAL FRACTIONS OF POM FROM THE EMS-DOLLARD ESTUARY

The Ems-Dollard estuary is located between the Netherlands and Germany and is part of the Wadden Sea, the coastal sea bordering the Netherlands, Germany and Denmark (Fig. 1). The main contributor of fresh water to the estuary is the river Ems, the Westerwoldse Aa is minor contributor. In the Ems-Dollard estuary marine and fluviatile particulate matter is accumulated. Transported by inward [5]. Adequate quantitative estimations of the absolute input of particulate matter from various sources, i.c. the rivers Ems and Westerwoldse Aa and the North Sea, are not available. Based on mineralogical analysis Favejee [6] concluded that particulate matter from the North Sea was the major source for sedimentation in the Dollard. The sedimentation rate in the Dollard is ca. 1 to 2 mm per year, but is the net result of inward transport and sedimentation and outward transport of resuspended sediment. Thus the Dollard as well as other shallow parts of the estuary act as an source for suspended matter.

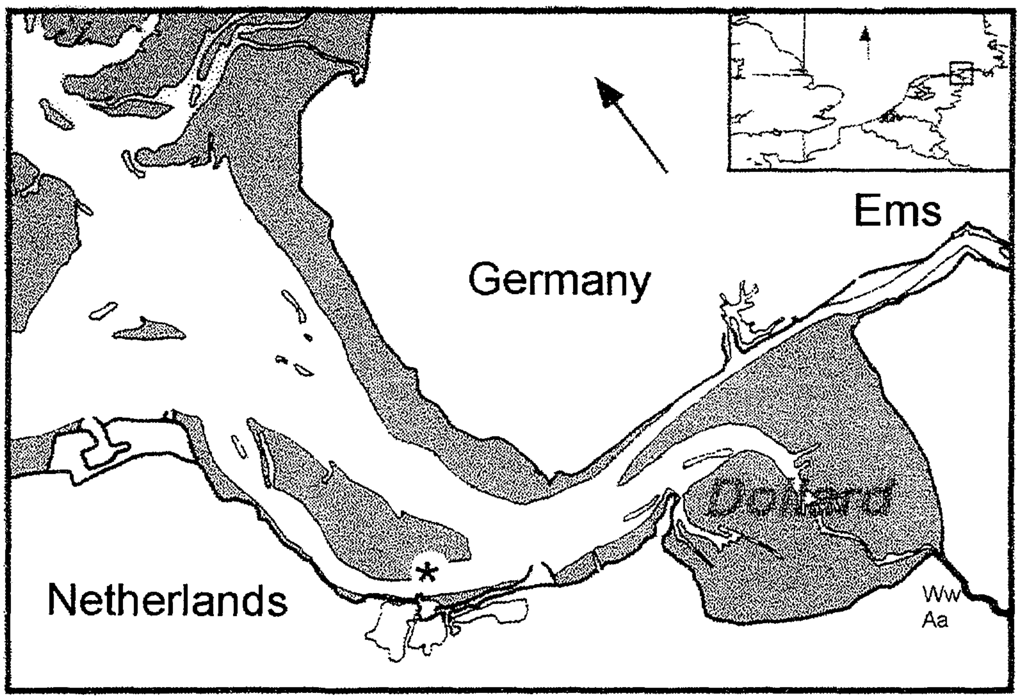

FIG.1 Map of the Elms-Dollard estuary. Asterisk indicates sample location.

In an attempt to overcome the problems when measuring just one parameter for the determination of the origin of POM, we combined stable carbon isotope analysis with radiocarbon dating and molecular characterization and analyzed not only bulk samples but also isolated chemical fractions (hot water extract, HCl hydrolysate, total extractable lipids, base hydrolyzed and extracted compounds and final residue) representing labile and refractive components in POM [7]. In a suspended POM sample from the Bocht the Bocht van Watum, a tidal channel in the middle part of the Ems-Dollard estuary (Fig. 1) large differences in both $\delta^{13}C$ and ^{14}a values between the different fractions were observed. Fractions consisting mainly of labile compounds like carbohydrates and amino acids (water extract and HCl hydrolysate) had considerably higher $\delta^{13}C$ and ^{14}a values than the residual material (differences ca. 4 ‰ and 50-60 pMC respectively). Lipids and base extracts had in-between ^{14}a values but $\delta^{13}C$ values similar to the $\delta^{13}C$ of the residual material. Chemical analysis showed that the residual OM consisted mainly of aliphatic macromolecular material which has a similar fractionation for ^{13}C as lipids. Therefore, the lower $\delta^{13}C$ value (-25.1 ‰) of this fraction appears not to indicate a higher terrestrial contribution, taking into account that the $\delta^{13}C$ of bulk POM from the fresh water part of the river is between -26 and -28 ‰ [8] and the $\delta^{13}C$ of the corresponding fraction would be several per mil lower. Fractionation due to different biosynthetic pathways can explain the lower $\delta^{13}C$ sufficiently. This conclusion is supported by the conclusion of Favejee [6] that suspended sediment from the river did not reach beyond the Dollard area.

3. ORGANIC MATTER IN SIZE FRACTIONS OF SURFACE SEDIMENT FROM THE EMS-DOLLARD ESTUARY.

Most OM in sediments is adsorbed to mineral particles [9] and the mineralogical composition might influence the kind of OM that is adsorbed [10 and references therein]. Large particles usually consist mainly of silica while fine particles contain high amounts of clay minerals which appear to have a higher affinity for charged amino compounds. We studied the influence of particle size on stable carbon, radiocarbon and molecular composition of OM in different size fractions [11] of a surface sediment from the same location as the above mentioned suspended matter sample. The fractions >20 µm had a considerably lower ^{14}a value (ca. 50 pMC) than the finer fractions (ca. 80 pMC), clearly showing the different origins of the material. The $\delta^{13}C$ values of the coarse fractions were lower as well, possibly indicating a larger contribution of a terrestrial source, but chemical analysis by means of pyrolysis-gas chromatography that the OM in the coarse fractions had a more lipidic nature, which also can explain the lower $\delta^{13}C$ values.

4. SEASONAL VARIATIONS IN $\delta^{13}C$ AND ^{14}a OF POC FROM THE EMS-DOLLARD ESTUARY

The main seasonal event in the Ems-Dollard is the occurence of algal blooms in spring and early summer which are strongest in the outer (seaward) and middle part of the estuary . Daily primary production during a bloom could be as high as 5-6 g C m^{-2}, compared to ca. 10 mg C m^{-2} during winter [12]. We studied the seasonal variation in the stable isotope ratios and ^{14}C concentrations in suspended POC from the Bocht van Watum, in the middle part of the estuary (Fig. 1). Samples were taken four times a year in 1992 and 1993.

In autumn and winter, when primary production in the estuary is low, the ^{14}a value of POM (average 75 ± 3 pMC) is quite similar to that of POM from the fresh water part of the Ems, but is rather low compared to DIC values in the estuary (ranging from 87 pMC in the river to 120 pMC or even higher in the North Sea) and ^{14}a values of POM from the North Sea (ca. 87 pMC). This shows that there is a considerable relatively old component in estuarine POM, probably originating from the river. The Ems is flowing through an area where peat was deposited since ca. 7000 years BP [13]. The oldest fraction from the previously analyzed [7] POM sample from this location had a ^{14}a value of 43 pMC which is equivalent to ca. 6800 years BP (the insoluble, non-hydrolyzable fraction).

The average $\delta^{13}C$ value of the autumn and winter samples is -23.2 ± 0.5 ‰. This value lies between $\delta^{13}C$ values of marine phytoplankton and of POM from the river but is also a typical value for POM from the Dutch coastal waters of the North Sea [8]. But since the ^{14}a values are different, autumn and winter POM at this location in the estuary is not the same as North Sea POM. It is also not a simple mixture of marine (North Sea) and fluviatile POM. A major source for suspended matter in the rather shallow Ems-Dollard probably is resuspended sediment. Unfortunately, few is known about the carbon isotope concentrations in sedimentary organic matter from the Ems-Dollard. OM in the sample of the upper 15 cm of the sediment at this location (from the bottom of the tidal channel) had a $\delta^{13}C$ of -23.9 ‰ and a ^{14}a of 71 pMC [11]. OM in the fraction <63 µm, which is probably more representative for resuspendable material [14], had a $\delta^{13}C$ of -23.5 ‰ and a ^{14}a of 74 pMC, both quite similar to the values of winter / autumn POM. Values of sediment from the tidal flats, which is the main source for resuspended sediment [14], are not available.

In spring 1993 we observed an increase in both $\delta^{13}C$ and ^{14}a values compared with autumn and winter samples. This indicates the increased contribution of phytoplankton to total POC, caused by the blooms around this time. The organic carbon concentration in the suspended matter increased as well, from ca. 3.5 % in winter / autumn samples to 5.2 % in the spring 1993 sample. Calculated from these organic carbon concentrations ca. 40 % of the organic carbon in the sample is derived from fresh phytoplankton. Using this latter value in a two component mixing equation for a mixture of fresh phytoplankton and suspended matter with the same characteristics as the winter and autumn samples, the $\delta^{13}C$ and ^{14}a values of the fresh phytoplankton would be -18.8 ± 1 ‰ and 106 ± 5 pMC respectively. The $\delta^{13}C$ has a value typical for marine phytoplankton, the ^{14}a is not significantly lower than known ^{14}a values of DIC in the North Sea [15]. Phytoplankton blooms in the Ems-Dollard estuary are considered to be autochthonous. However, the calculated isotope values for the phytoplankton in this sample are somewhat different from what might be expected based on DIC values in this part of the estuary. The discrepancy between the calculated carbon isotope concentrations of the algae in the sample and DIC values might be due to inaccuracies in the used parameters or calculation.

The sample from spring 1992 shows a small increase in it's ^{14}a value, much less than the spring 1993 sample. The $\delta^{13}C$ value is even a little lower than the average autumn/winter value. The higher ^{14}a value points again to an increased contribution of fresh material to the POM, for which a phytoplankton bloom is the most likely cause. However, in that case it would also be expected that the $\delta^{13}C$ value would be higher.

The $\delta^{13}C$ of DIC in the Ems-Dollard ranges from -11 ‰ in the river Ems to ca. 0 l in the North Sea. The ^{14}a ranges from 87 pMC in the river to ca. 120 pMC in the outer part of the estuary. Thus, if the inorganic carbon source for the algae in spring 1992 contained more fluviatile DIC than in 1993, it is possible to cause an increase in the ^{14}a value of the total POM and a decrease in it's $\delta^{13}C$. Analysis of labile organic fractions or compounds specific to algae will be needed to yield conclusive evidence.

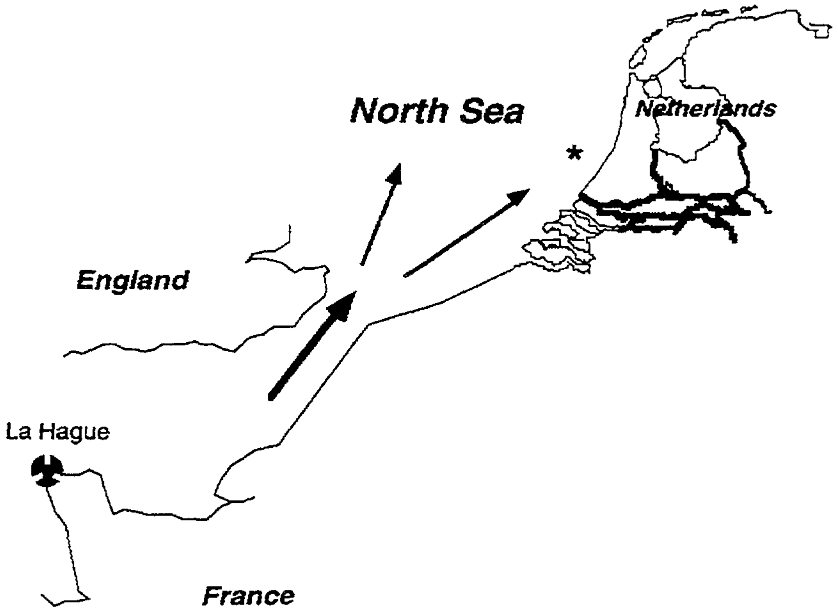

FIG. 2 Map of the North Sea. Sample location marked by an asterik.

5. POM AND PHYTOPLANKTON IN THE SOUTH-EAST NORTH SEA

The southern North Sea, the shallow shelf sea between the Netherlands and the British Isles, receives particulate matter from the English Channel, the northern North Sea and the rivers. Input of suspended matter through the Channel is estimated to over 10 million ton dry weight per year and of the rivers ca. 4.5 million ton [16]. Supply of total organic matter was estimated to 0.6 million ton per year from the Channel, 0.4 million ton from the northern North Sea (north of 54E latitude) and 2.5 million ton from the rivers [17]. Concentrations of suspended matter are highest in the Dutch and Belgian coastal waters in the East and of East Anglia in the West. This might lead to the hypothesis that the rivers are the main sources for suspended matter, but due to the circulation pattern suspended matter is concentrated in the coastal areas because residual currents bring bottom water to the shore [16].

An attempt to directly determine the origins of suspended matter off the Dutch west coast was made by Salomons and Mook [18], using stable carbon and oxygen isotope ratios in the inorganic carbonate fraction. Analyzing stable carbon isotope ratios and radiocarbon concentrations in the organic fraction, we tried to determine the origins of the POM.

Suspended matter samples from February and November 1994 consisted mainly of inorganic material with associated organic matter, while the May and August samples consisted almost completely of fresh phytoplankton, due to extensive blooms and low resuspension at the time of sampling. The ^{14}a value of the phytoplankton in these samples is 120 pMC, rather high compared to ocean DIC values and atmospheric CO_2 (both ca. 110 pMC). The same high value of 120 pMC was measured in DIC from the German Bight [15] and in DOC from the Frisian Front [19]. Le Clercq et al. [15] suggested that the high ^{14}a in DIC from the German Bight was caused by nuclear energy related activities along the Elbe, which discharges in the German Bight. The water in front of the Dutch coast comes mainly from the English Channel, where at La Hague in Normandy a nuclear fuel reprocessing plant is located. Recent measurements in our laboratory of terrestrial plant leaves that grew near the facilities, showed that they were almost 8 times enriched in ^{14}C (780 pMC). It is not unlikely that this nuclear facility causes an enrichment in DIC in the sea water as well, as is the case in the Irish Sea due to the reprocessing plant in Sellafield [20,21].

In February and November ^{14}a values are much lower indicating the higher contribution of older organic material. The higher ^{14}a value of the November sample compared to the February sample, combined with a higher δ^{13}C value, shows that this sample still contains ca. 35 % fresh phytoplankton derived material. The February sample has a δ^{13}C value of B23.2 l which is typical for POM from this area of the North Sea [8]. The δ^{13}C appears to indicate a mixture of terrestrial and marine material. However, when both δ^{13}C and ^{14}a are compared with the available data from POM from the Rhine and Meuse, it appears that this POM is not a mixture from riverine (terrestrial) POM and fresh marine POM. Salomons and Mook [18] already concluded that the contribution of inorganic particulate carbonates from the rivers was negligable. Thus virtually all the POM in the coastal water is resuspended sediment.

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THE AMS ANALYSIS OF ^{129}I AND ^{135}Cs: DEVELOPMENT OF TOOLS FOR OCEANOGRAPHIC TRACING AND POLLUTION SOURCE IDENTIFICATION

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Abstract:

The development of the accelerator mass spectrometer analysis of ^{129}I and its applications to oceanographic tracing from the point source releases by nuclear fuel reprocessing plants is reviewed. Some new data for ^{129}I concentrations in the Mediterranean Sea are presented. The uses of Cs isotope information in conjunction with ^{129}I data is examined and two possible strategies for the analysis of Cs isotopes by AMS are discussed: a) the sputtering of Cs^+ ions using negative sputtering beams followed by charge changing to negative ions and b) the use of a resonant transfer canal to produce Cs^-.

1. INTRODUCTION

The ability to measure ^{129}I (half life 1.57 × 10^7 a) at natural non-anthropogenic concentrations (~ 10^9 atoms/g) insmall (mg sized) samples by accelerator mass spectrometry (AMS) was demonstrated shortly after the initial development of AMS for ^{14}C [1]. A limited number of applications were investigated, for example, hydrology [2] and the characterization of oil reservoirs [3], but the expense of analysis using large tandem accelerators precluded applications requiring large numbers of measurements. In 1987, Kilius [4] demonstrated the detection of ^{129}I using a smaller system designed specifically for ^{14}C analysis, without the requirement of time-of-flight measurements after the accelerator. However, two modifications to this system were required:

a) the addition of electric analysis before the accelerator. This was required to reduce the high energy tail of the ^{127}I ion beam caused by the sputter source and to remove some hydride interferences, and,

b) the installation of a magnet with higher mass-energy product and an additional electric analyser sfter the accelerator.

Following this demonstration, the IsoTrace Heavy Element Analysis line was designed and installed [5], with high resolution magnetic (M/ΔM = 2600) and electric (E/ΔE = 900). The first routine measurements of ^{129}I with this system were for a survey of ^{129}I concentrations in both archived (pre weapons testing) and contemporary samples, with a number of these of marine origin (kelp) [5,6]. This survey showed an average of two orders of magnitude difference between the archived and contemporary materials.

2. USE OF ^{129}I AS A MONITOR OF NUCLEAR FUEL HANDLING

As ^{129}I is a relatively mobile fission product, known to be released during the reprocessing of nuclear fuel material [7], testing of materials from the vicinities of reprocessing plants soon followed.Raisbeck and Yiou collected both kelp and water samples from the English Channel near Cap la

Hague [8]. Kilius and Rucklidge analysed kelp samples from the Pacific north west coast of North America to assess the transport of ^{129}I from the Hanford reprocessing facility [9]. Samples obtained over a range from 1000 km south to 1000 km north of the Columbia River estuary showed a ^{129}I /^{127}I ratio with an approximately symmetrical distribution on either side of the estuary. The peak at the estuary was ~ 20 times the average fallout level, but three orders of magnitude below the level from Cap la Hague.

On an oceanographic scale, these reprocessing plants were effectively point sources of a uniquely identifiable material. The feasibility of using ^{129}I as a tracer for ocean currents downstream from these plants was demonstrated by Yiou *et al* [8,10]. With samples obtained in the North Sea, along the Norwegian coast and as far as Svalbard, they showed that 1 l of water was sufficient to observe the ^{129}I /^{127}I ratio signal from Sellafield and Cap la Hague and included some data which illustrated the process of deep water formation. With the release of the Yablokov report documenting the location and contents of nuclear waste disposal sites in the Arctic [11] raising concern about contamination in the Arctic, additional ^{129}I, in conjunction with ^{137}Cs measurements in the Barents and Kara Seas showed that the European reprocessing plant signal dominated any other source at that time [12].^{129}I was also used to trace the reprocessing plant signal through the areas of deep water formation off Greenland [13].

3. USE OF ^{129}I AS A TRACER OF ARCTIC OCEAN CIRCULATION

Applications of ^{129}I tracer techniques to oceanographic studies of water circulation (measurements of ^{129}I) have continued at the IsoTrace Laboratory despite the untimely death of Dr. L. R. Kilius [14] who had contributed so much to the development of this technology. As much of this work is the subject of recent publications [15-20], and other presentations at this conference [21-22], it is summarized in Table 1. With these measurements the advance of warmer but denser Atlantic water under the Arctic ice cap is being monitored by sampling from submarines and surface vessels.

TABLE I: ^{129}I SAMPLES FROM THE ARCTIC AND NORTH ATLANTIC ANALYSED AT THE ISOTRACE LABORATORY 1994-1997

Year	Cruise	Region	Number of Samples Analysed
1994	CSS Louis St. Laurent USS Polar Sea	Transect: Bering Straight -- Pole -- Fram Straight	86
1995	SCICEX95: USS Cavalla	Central, Western Arctic	146
	CSS Louis St. Laurent	Beaufort Sea	99
1996	CSS Hudson	North Atlantic	46
	SCICEX96: USS Pogy	Central, Western Arctic	147
1997	CSS Hudson	Labrador Sea	124
	SCICEX97: USS Archerfish	Central, Western Arctic	139
	CSS Louis St. Laurent	Canadian Arctic Archipelago	20

4. PRESENCE OF ^{129}I IN THE MEDITERRANEAN

In addition to the measurements of ^{129}I in the Arctic and North Atlantic, a survey in the Western Mediterranean was carried out by Yiou *et al* [23]. High values were found in the Rhône estuary which led the authors to conclude that the reprocessing plant at Marcoule was the probable source, but that it was emitting ~ 300 times less ^{129}I than the plant at Cap la Hague. ^{129}I concentrations measured in coastal waters east of the estuary were typically ~ 5×10^8 atoms/l.

During an investigation of the ^{129}I content of water from a hydrothermal vent in the Aegean Sea by SWF and JCM, a surface sample of water from a location off the west coast of the island of Milos was measured as a control. The ^{129}I concentration in this sample, was also elevated: 4.12×10^8 atoms/l, approximately an order of magnitude higher than the value expected from weapons tests. Surface water in this location comes from the western Mediterranean basin, so it is likely that the ^{129}I may have come from the Rhône. Two additional samples were obtained off the coast of Monaco; their concentrations are reported in Table 2.

TABLE II: RECENT ^{129}I MEASUREMENTS IN THE MEDITERRANEAN

IsoTrace Number	Sample Identification	^{129}I Concentration *(× 10 atoms/l)*
TOI-3452	Milos Island "Control"	4.12 ± 0.15
TOI-4164	Monaco Station A	2.87 ± 0.10
TOI-4165	Monaco Station B	3.01 ± 0.11

These latter concentrations are ~ 60% of that measured in the eastern-most measurement by Yiou *et al* [23] which was obtained ~ 20 km away and 5.5 years earlier. This reduction, if significant, could be evidence of the decrease in activity at Marcoule mentioned by Yiou *et al*. Further investigations in the Mediterranean would be of interest.

5. ADDITIONAL INFORMATION FROM CAESIUM ISOTOPES

A concentration of ^{129}I significantly higher than the fallout value in a sample of sea water provides, in addition to tracer information, an estimate of the amount by which the water (and its other isotopic components) from the source have been diluted in that sample. If another isotope from the source, e.g. ^{137}Cs has been transported along with the ^{129}I, the reduction in ^{137}Cs concentration with respect to ^{129}I concentration can yield the transit time from the source to the sampled area [19]. Current methods of ^{137}Cs analysis require ~ 20 l of water; this is too large for sampling on the same scale as ^{129}I when using submarines for collection. In addition, as more time elapses since the generation of the ^{137}Cs, the signal becomes weaker and larger samples are required. Eventually, all of the fallout ^{137}Cs in the natural environment will be undetectable by gamma counting and the only way to continue to measure fallout Cs will be by the AMS detection of ^{135}Cs

For short transit times, other Cs radioisotopes such as ^{134}Cs have provided additional data for identification of the source, but due to its half life of 2 years, it is of limited value. ^{135}Cs has a longer half life (3×10^6 years), but, like ^{129}I, cannot be measured by decay counting. Furthermore, because of the large neutron cross section for 135Xe, the ratio of ^{135}Cs /^{137}Cs will be characteristic of the reactor operating and shutdown conditions. This may be an advantage in identifying the source of the Cs, however, this requires that measurements of this ratio be made, e.g. in sediments near the reprocessing plant, to establish the time dependence of this ratio.

The detection of ^{135}Cs from fallout in sediments has been demonstrated by Lee *et al* [24], using thermal ionization mass spectrometry with the addition of an electrostatic filter. They observed interference from Ba isotopes and minimized it by running the filament at a lower temperature (700°C) and monitored this by measuring masses 136 and 138 as well. However, this is a difficult measurement to carry out as the levels of ^{135}Cs from fallout were 10^{-9} of the level of the ^{133}Cs in the sediment sample and only with the electrostatic filter could the tail from ^{133}Cs isotope be removed.

6. AMS ANALYSIS STRATEGIES FOR CAESIUM

6.1. Initial Cs measurements using AMS

The considerations noted in section 5 have motivated a study of the feasibility of measuring Cs isotopes by AMS at IsoTrace. Initial studies by Kilius showed the presence of an interference from Ba isotopes of the same mass; this measurement was confirmed recently by one of us (XLZ). A sample of analytical grade CsI was mixed with Nb powder, pressed into a 3 mm diameter sample holder, heated for 1 h in air to remove water vapour and inserted into the sputter source of the IsoTrace accelerator mass spectrometer. A beam of ^{133}Cs^{+4} was selected and a current of 8 particle pA was measured in the Faraday cup following the last electric analyser on the Heavy Element Line. Without changing the sample, the low and high energy magnetic analysers where adjusted to pass mass 137; 149 particle counts were observed in 500 s. To confirm that this interference was 137Ba, the system was adjusted to pass mass

138 and the counting ratio of mass 137 to mass 138 observed was appropriate for the abundances of these Ba isotopes. This measurement indicated a ^{137}Ba contamination in the Cs at a level of 6×10^{-9}, but could not distinguish between Ba contamination of the CsI target or the Cs used to generate the sputtering beam.

6.2. Generation of Cs^+ followed by charge neutralization

A technique for the analysis of non-conducting geological samples is currently being developed at IsoTrace [25]. To avoid the instability problems which occur during the positive ion sputtering of insulators, this technique uses a negative sputtering beam, such as O^-, Cl^-. I^- or Au^-, and positive ions are extracted from the sample. For normal AMS analysis, these ions would simply be charge changed, energy and momentum analysed and transported to the accelerator.

Figure 1 shows how this equipment would be configured for the analysis of Cs, in the form of a target made of Cs_2O. As the source for the negative sputtering beam also uses Cs (a modified High Voltage Engineering Model 860 source), mass analysis of the negative sputtering beam is needed to remove any Cs^- from the beam. The Cs^+ from the sample is then resonantly charge neutralized [26] in a Cs vapour canal at -40 kV. This process is expected to remove the majority of the Ba interference; if too much remains, an additional magnetic field for charge separation can be used. The beam of Cs° can then be used directly in a neutral injection AMS machine [27] or charge changed to negative in a standard Li vapour canal for conventional AMS.

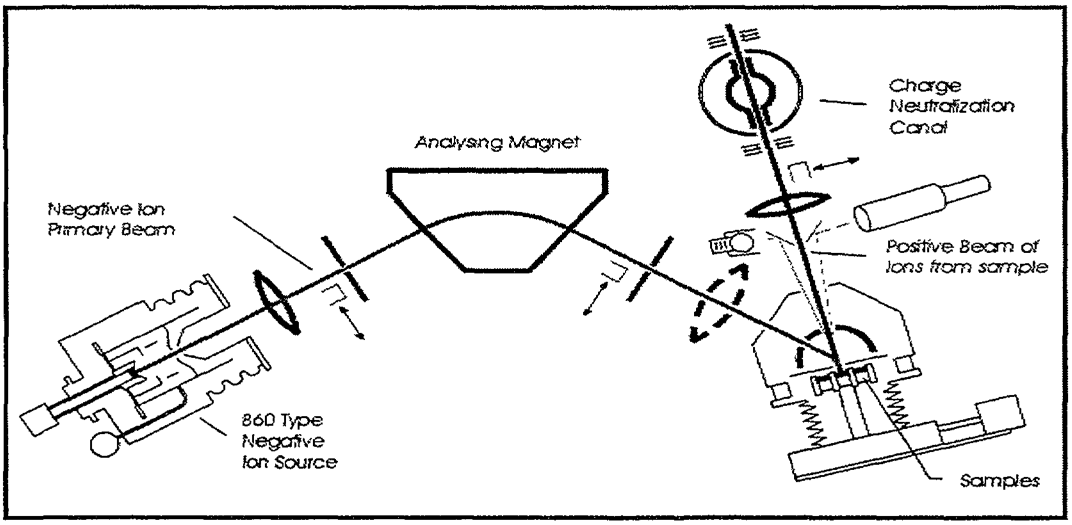

Figure 1: Configuration of the equipment for Cs analysis as described in section 6.2.

6.3 Generation of Cs^- by resonant electron transfer.

A more elegant method of generating Ba free beams from a Cs sample has been proposed by Litherland *et al* [28]. In this method, the sample material is vapourized in a canal, in a manner similar to the ionization of the sample from a filament in thermal ionization mass spectrometry. A beam of Cs^- is incident on the vapour from the sample in the canal and produces Cs^- from the sample material by electron transfer. The Cs^- from the sample is separable from the Cs^- in the incident beam by their difference in momentum (the momentum of the incident beam). If the sample canal is run at ~ 100°C, the presence of Ba in the vapour will be strongly inhibited. As this method requires somewhat more challenging hardware development, the approach in section 6.1.2 is being examined first.

7. CONCLUSIONS

The AMS analysis of ^{129}I from small samples of seawater has provided a useful tool for the tracing of ocean circulation in regions where influx from point sources of this isotope exists, even at great distances from the source. The analysis of ^{137}Cs in parallel with the ^{129}I provides information on transit times as well as some identification of the source of these isotopes. With the gradual disappearance of ^{137}Cs both from fallout and from reprocessing plant discharges, there is a need to find a technique which can provide similar information; the AMS analysis of Cs isotopes would extend the time through which ^{137}Cs remains useful and permit the use of ^{135}Cs as a replacement.

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MEASUREMENTS OF RADIOCARBON IN THE NW PACIFIC OCEAN AND ITS MARGINAL SEAS

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Abstract

Radiocarbon is an important tracer in the oceans. Small amounts of radiocarbon can easily be measured by accelerator mass spectrometry on mg-sized samples of carbon extracted from 250 ml water samples. Dumping of liquid and solid radioactive wastes at sites in the NW Pacific Ocean and its marginal seas can be a potential source of radiocarbon contamination in the oceans. The purpose of this paper is to discuss some preliminary measurements designed to study this problem.

1. INTRODUCTION

Over the past 10 years, reports of radioactive waste dumping at sea have become well documented. IAEA [1] compiled information on inventories of radioactive wastes dumped by European countries in the NE Atlantic Ocean, by the USA in the NW Atlantic and NE Pacific Ocean, by New Zealand in the SW Pacific Ocean, by Japan in the NW Pacific Ocean, and by the Republic of Korea in the Sea of Japan/East Sea. In 1993, moreover, the White Book revealed that large quantities of radioactive wastes had been dumped in the Kara and Barents Seas and the NW Pacific Ocean and its marginal seas by the former USSR and that smaller amounts of radioactive wastes had been dumped later by the Russian Federation [2].

Since 1994, IAEA's Marine Environment Laboratory (IAEA-MEL) has been engaged in an assessment programme related to radioactive waste dumping in the NW Pacific Ocean and its marginal seas. IAEA-MEL participated in the Japanese-Korean-Russian joint expeditions in 1994 and 1995 to the dumping areas in these regions, and also took part in analysis of anthropogenic and natural radionuclides in seawater and sediment samples collected during the expeditions [3, 4]. An important factor in the assessment of potential releases from radioactive wastes is the efficient measurement of small samples collected at or near the dumping sites. In this paper, we report on methods and give some preliminary results of ^{14}C analysis of seawater samples collected near dumping sites and in the open ocean.

2. METHODS

Seawater samples were collected for ^{14}C measurements during the second Japanese-Korean-Russian joint expedition 1995 [5] and the IAEA '97 Pacific Ocean Expedition 1997 [6]. The sampling stations are shown in Fig.1. In the first expedition, stations R3 and/or R4, J3 and K1 were selected in areas where radioactive wastes had been dumped in the past by the former USSR and/or the Russian Federation, Japan and the Republic of Korea. At Station R2, a ^{90}Sr source of 13 PBq was accidentally lost. Stations BG1 and BG2 are outside the dumping areas, reflecting background levels. In the IAEA Pacific Ocean Expedition, all samples were collected in the open ocean, although Stations 6 and 7 are close to Bikini and Enewetak atolls, former nuclear weapons testing sites.

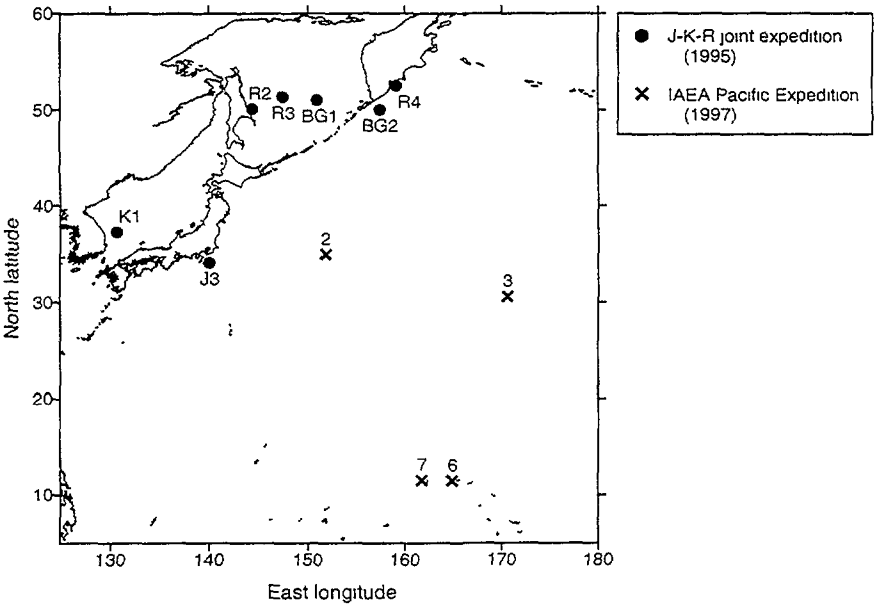

FIG.1. Sampling stations for ^{14}C measurements in seawater collected during the second Japanese-Korean-Russian joint expedition and the IAEA '97 Pacific Ocean Expedition

During the expeditions, seawater samples of approximately 0.5-1 liter were collected in glass bottles. $HgCl_2$ was added to the samples to stop further biological activities. These samples were shipped in sealed containers directly by air freight from Japan to the University of Arizona. In the laboratory, the dissolved inorganic carbon (DIC) was extracted by acidification of the sample water to pH 3 and the carbon dioxide released was extracted in a flow of high-purity oxygen gas. The CO_2 was purified by passing the gas through cryogenic traps to remove water, and Cu/Ag to remove nitrogen oxides and halogens. The stable-isotopic composition of a split sample of the gas was measured in an Optima mass spectrometer, and the remaining gas was converted to graphite over an Fe catalyst, as described by Donahue et al. [7].

3. RESULTS

Radiocarbon activity in seawater samples is expressed by $\Delta^{14}C$ which is defined as:

$$\Delta^{14}C\ (‰) = (\,Fm - 1\,) \times 10^3$$

where Fm (a fraction of modern carbon) is the measured AMS ratio of ^{14}C to ^{13}C, normalized to $\Delta^{13}C$ of -25 ‰, as defined by Donahue et al. [8].

Fig. 2 shows the spatial distribution of radiocarbon activity in surface and bottom waters. A latitudinal tendency can be observed in the surface water values although the number of data is limited. The concentration is relatively low in the subarctic region at a higher latitude, increasing toward the subtropical region at a median latitude, and decreasing again in the tropical region of the Pacific Ocean. High concentrations are observed at Station J3 south of the Main Island of Japan and at Station K1 in the Sea of Japan/East Sea, which are close to the sites where radioactive waste was dumped by Japan and the Republic of Korea. The cause of the high activity in surface water must be further investigated using a larger number of data since these two stations are located in the strong surface Kuroshio Current and on the edge of the Tsushima Current, respectively.

The radiocarbon activity in bottom water, on the other hand, differs from that in surface water. The activity concentration tends to depend on the total depth rather than on latitude. The concentrations in deeper areas of the Pacific Ocean have similar values although the level at Station 7, close to Enewetak atoll, is slightly higher. Seawater at Station J3 shows the same concentration as Stations R3 and BG1 in the Sea of Okhotsk, where the depths are almost the same as J3. The levels at Stations R4 and BG2, south of Kamchatka Peninsula, have intermediate values between those of deeper areas of the Pacific Ocean and those in the Sea of Okhotsk, as the depths at R4 and BG2 are also intermediate. However, the concentration at Station R2, east of Sakhalin Island, is high, probably because the station is in shallow coastal water. Bottom water at Station K1 has a high concentration of radiocarbon although the sea is rather deep (2100 m). The radiocarbon activity at Station K1 is high in both surface and bottom waters, which could be due to a leakage from the dumped wastes. Unfortunately, the activity and composition of the wastes dumped in the Sea of Japan (K1 area) are not well known.

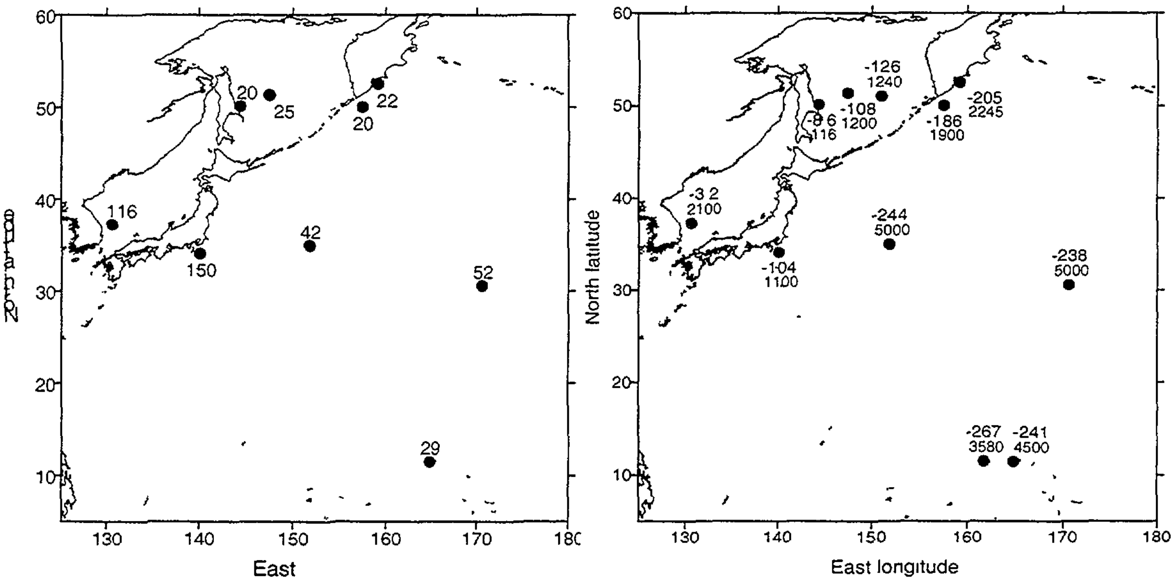

FIG.2. Radiocarbon activity in $\Delta^{14}C$ (‰) in surface water (left) and bottom water (right) in the NW Pacific Ocean and its marginal seas.
(For the bottom water, $\Delta^{14}C$ (‰) and a sampling depth (m) are shown.)

Fig.3 shows vertical profiles of radiocarbon activity at 4 sampling stations in the open ocean of the NW and Central Pacific Ocean. Generally the profiles are typical for the North Pacific Ocean, and similar to those reported by the WOCE group [9]. The activity shows an excess in surface water, decreasing sharply with depth down to 1000 m, and reaches a minimum at 2000 to 3000 m depth, increasing gradually to the bottom. The excess value in surface water indicates that it is influenced by bomb-produced radiocarbon. In Stations 2 and 3 at median latitudes, a small and sharp depression in the concentration is observed at around 130 m and 200 m depths, respectively. These depressions may be caused by processes which require further investigation.

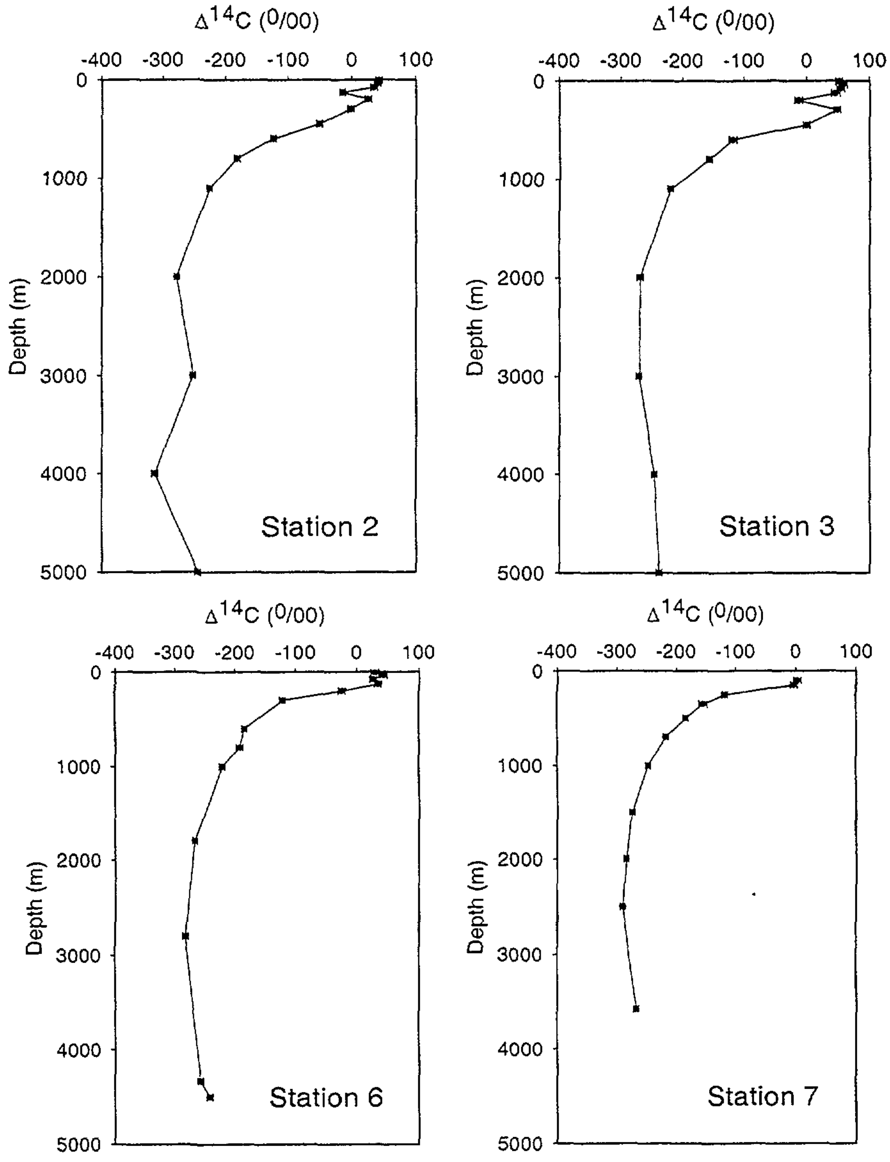

FIG.3. Vertical profiles of $\Delta^{14}C$ at 4 sampling stations in the IAEA '97 Pacific Ocean Expedition

4. DISCUSSION

In the NW Pacific Ocean and its marginal seas, the concentration of other main anthropogenic radionuclides (^{90}Sr, ^{137}Cs and ^{239,240}Pu) in surface seawater generally has a similar tendency to that of radiocarbon [10, 11]. This is due to a latitudinal effect in which the concentration is relatively low in the subarctic region and the Oyashio Current region of a higher latitude, increasing toward the subtropical region of a middle latitude, and decreases again in the Central Pacific Ocean of a lower latitude. The activity in the Sea of Japan, on the other hand, is higher than in the subarctic region and the Oyashio Current region of the same latitude. These unique distributions could be partly explained by the geophysical processes occurring in these regions and by a possible additional input from close-in fallout transported from the Central Pacific Ocean [11, 12]. Further investigations are needed to develop a better understanding of the oceanic and geophysical processes affecting the similar spatial distribution of radiocarbon and other anthropogenic radionuclides in these regions.

High radiocarbon activity is observed in both of surface and bottom waters at Station K1 in the Sea of Japan/East Sea and in surface water at Station J3 in the south of the Main Island of Japan. The high concentrations indicate that a radiocarbon source may exist in these regions. Station K1 especially, may indicate some leakage from dumped radioactive wastes. Unfortunately, information available on the activity and composition of wastes dumped in the area K1 is very limited. Dumped low activity solid wastes were expressed only by a surface dose rate of 0.1-46 mR/h [1]. At the present, however, it is difficult to derive a definite conclusion since the number of data is still very limited. In order to investigate the cause in detail, a larger number of results are needed, especially those in the Sea of Japan and the Kuroshio Current region.

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We are grateful to the Governments of Japan, the Republic of Korea and the Russian Federation for the invitation to participate in the Japanese-Korean-Russian joint expeditions. The IAEA '97 Pacific Ocean Expedition was conducted within the framework of a five-year project MARS, supported by the Science and Technology Agency of Japan. Cruise participants who assisted in sampling of small water samples are highly acknowledged. IAEA-MEL operates under a bilateral agreement between the IAEA and the Government of the Principality of Monaco.

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IAEA-SM-354/109

PLUTONIUM ISOTOPE RATIOS IN ENVIRONMENTAL SAMPLES FROM THULE (GREENLAND) AND THE TECHA RIVER (RUSSIA) MEASURED BY ICPMS AND α-SPECTROMETRY.

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Abstract

Plutonium, americium and neptunium isotope ratios from the marine environment at the Thule nuclear weapons accident site and the river system draining the Russian nuclear weapons production facility "Mayak" in the Urals are presented. The measurements are made by traditional α spectrometry (^{238}Pu/$^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu) and by mass spectrometry (^{240}Pu/^{239}Pu and ^{237}Np/^{239}Pu). Specifically for the Thule accident it appears clear, that the lost plutonium was not of one homogeneous quality and that it was not homogenised in the explosion and the fire following the accident. The ^{240}Pu/^{239}Pu atom ratio is seen to decrease in the order Palomares > Thule > Mayak.

1. INTRODUCTION

Ratios between isotopes of the same element as well as between different elements is a much used tool in environmental radioactivity studies. Common examples for anthropogenic radioactivity are ^{134}Cs/^{137}Cs, ^{90}Sr/^{137}Cs, ^{129}I/^{99}Tc and the four ratios we will discuss here: ^{238}Pu/$^{239+240}$Pu, ^{241}Am/$^{239+240}$Pu, ^{240}Pu/^{239}Pu, and ^{237}Np/^{239}Pu. There are various reasons for using the different ratios such as e.g. source identification and transit time estimates. As sufficiently sensitive mass spectrometers have become more common, the accuracy of several isotope ratio determinations have increased considerably, and this will probably lead to increased focus on atom ratios as a tool.

We will here present results from two widely different areas we have had the opportunity to study recently: the marine environment at the Thule nuclear weapons accident site and the river system draining the Russian nuclear weapons production facility "Mayak" in the Urals. The measurements are made by traditional α spectrometry (^{238}Pu/$^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu) and by

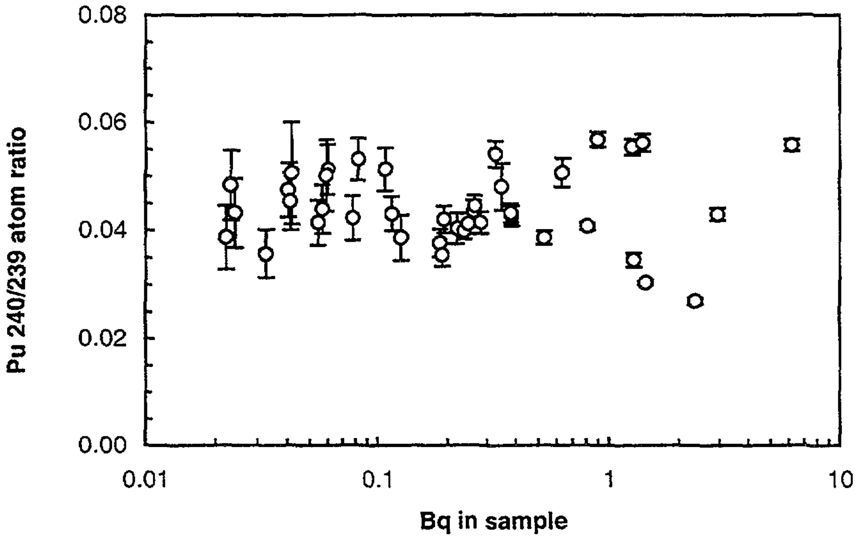

FIG. 1. ^{240}Pu/^{239}Pu atom ratios in sediment samples from the Thule site.

mass spectrometry (^{240}Pu/^{239}Pu and ^{237}Np/^{239}Pu.) using Risø's HR-ICPMS facility [1]. ^{237}Np have been analysed as described by Chen et al. [2].

2. THE THULE SITE

January 1968, a B52 plane carrying 4 nuclear weapons caught fire and crashed on the sea ice in Bylot Sound off Thule Air Base, northwest Greenland. It has been estimated from sample collections, that the pollution remaining in the seabed in Bylot Sound by 1968 amounted to approximately 1.4 TBq ^{239,240}Pu (~0.5 kg), 0.025 TBq ^{238}Pu, 4.6 TBq ^{241}Pu and 0.07 TBq ^{241}Am [3,4].

Mitchell *et al.* [5] suggested that the Thule material consisted of plutonium from at least two sources with significantly different isotope ratios. This conclusion was based on only one biased isotope ratio out of 5 relatively strong samples (0.6-6 Bq) measured with alpha spectrometry and

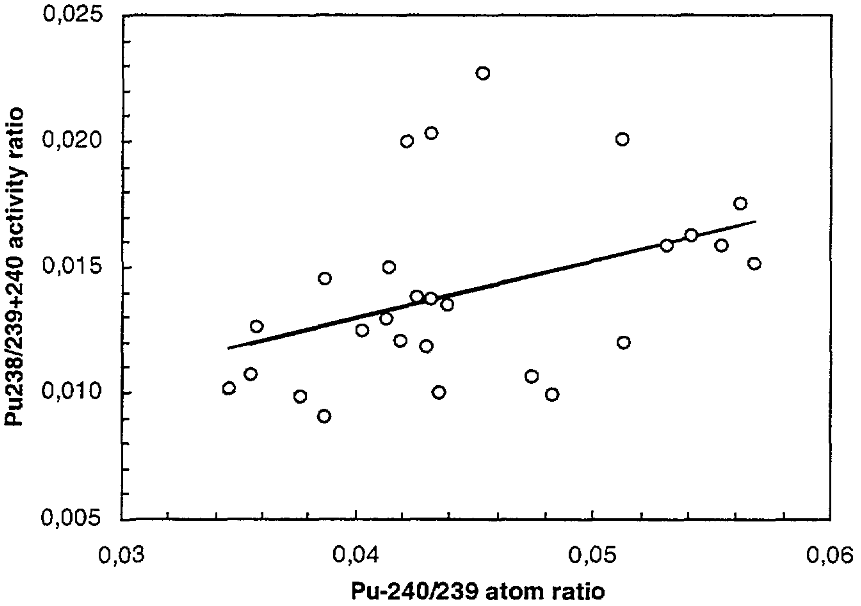

FIG. 2. Thule sediment samples 1997. ^{238}Pu/$^{239+240}$Pu activity ratios shown as a function of ^{240}Pu/^{239}Pu atom ratios. The regression line: $y = 0.0038 + 0.229\,x$ is probably significant (P>95%)

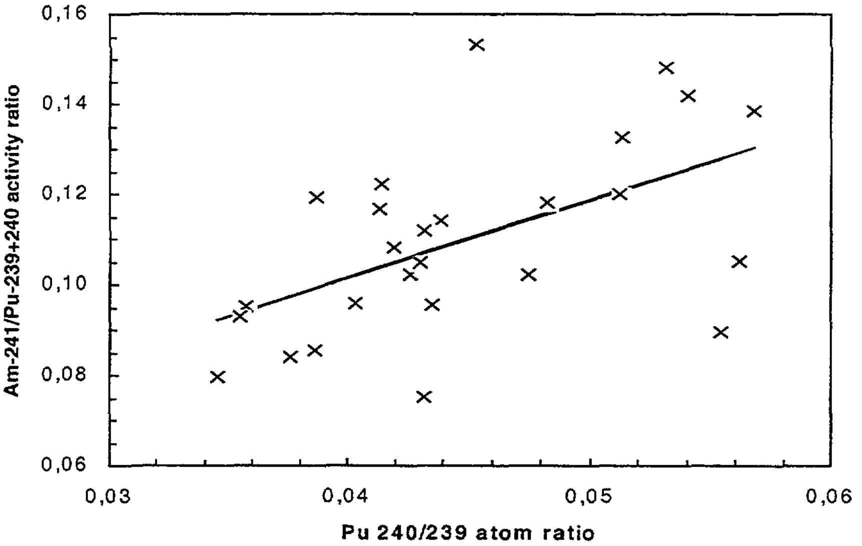

FIG. 3. Thule sediment samples 1997. ^{241}Am/$^{239+240}$Pu activity ratios shown as a function of ^{240}Pu/^{239}Pu atom ratios. The regression line: $y = 0.0327 + 1.72\,x$ is significant (P>99%)

spectral deconvolution. The same 5 samples were later measured at Risø's HR-ICPMS facility confirming Mitchell et al.'s observations. At present 40 Thule sediment samples taken 1979, 1991 and 1997 show $^{240}Pu/^{239}Pu$ atom ratios in the range 0.027-0.057 (Figure 1). Calculated uncertainties on most of the samples are 2 - 10 %. It is then concluded, that there is a variation in plutonium isotope ratios in the samples are 2 – 10%. It is then concluded, that there is a variation in plutonium isotope ratios in the Thule debris significantly above measurement errors. In Figure 1, it is seen that the stronger samples – which have all been identified as "hot particles" – show significantly different $^{240}Pu/^{239}Pu$ atom ratios. This supports the earlier conclusion [5] that the Thule plutonium originates from at least two sources of different quality. The intermediate levels may be either a third source or mixtures. Hot particles analysed from the Palomares accident are comparable to the highest $^{240}Pu/^{239}Pu$ atom ratios or even higher than the present Thule material [5].

In Figures 2 and 3, $^{238}Pu/^{239+240}Pu$ and $^{241}Am/^{239+240}Pu$ activity ratios are shown as a function of $^{240}Pu/^{239}Pu$ atom ratios. The data in figures 2 and 3 are all from the 1997 Thule sampling. Linear regressions show that the relationship between the $^{238}Pu/^{239+240}Pu$ and the $^{240}Pu/^{239}Pu$ ratios are probably significant (P>95%) and between the $^{241}Am/^{239+240}Pu$ and the $^{240}Pu/^{239}Pu$ ratios are significant (P>99%). This further supports the hypothesis that the Thule plutonium is not a homogeneous source, but rather consists of at least two different plutonium products with different production characteristics.

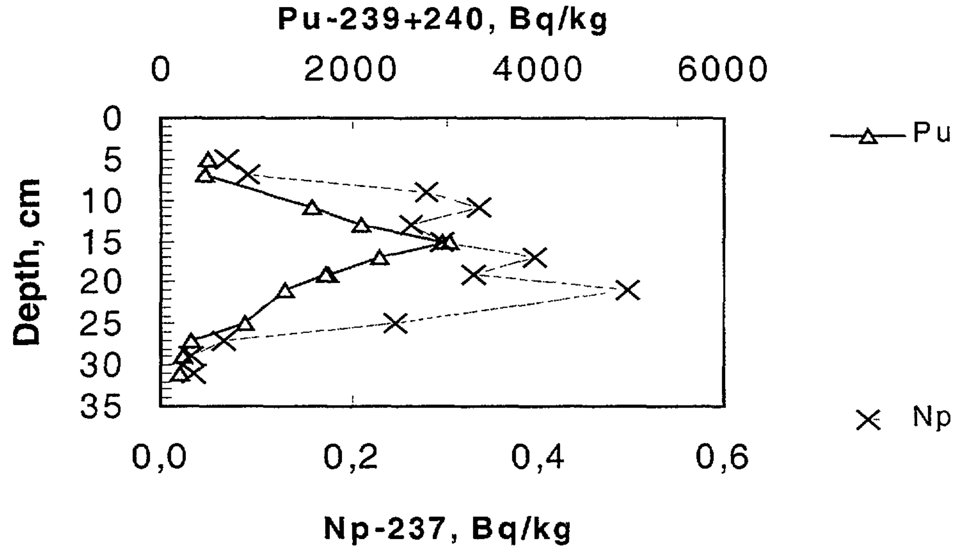

FIG. 4. Nadirov Bridge, Techa River 50 km from Mayak. Depth distribution of $^{239+240}Pu$ and ^{237}Np activity concentrations

3. THE MAYAK DRAINAGE AREA IN THE URALS

The river system draining the Russian nuclear weapons production facility "Mayak" in the Urals has received a variety of radionuclides from the production and processing of weapons plutonium from the late 1940's and onwards. Discharges include scheduled as well as accidental releases. [6,7]

Figures 4 and 5 show depth distributions of activity concentrations and atom ratios for plutonium and neptunium in a Techa River sediment core taken at Nadirov Bridge approximately 50 km downstream from the release point to the Techa River from the Mayak complex. Other radionuclide data from this core are given elsewhere [8,9]. It is seen that although there is a considerable variation in concentrations with depth, the $^{240}Pu/^{239}Pu$ atom ratios are very stable with depth, or in other words, with time. The average $^{240}Pu/^{239}Pu$ atom ratio show a remarkably low variation of the same size as the

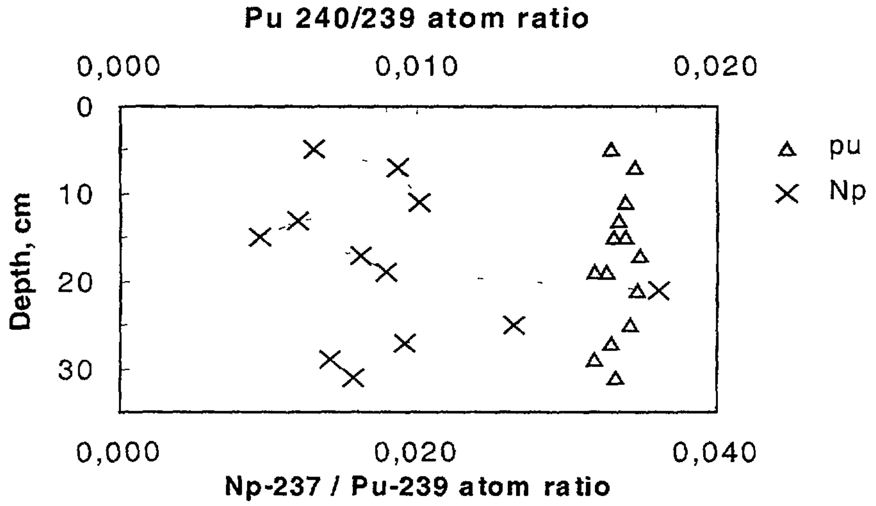

FIG. 5. Nadirov Bridge, Techa River 50 km from Mayak. Depth distribution of $^{240}Pu/^{239}Pu$ and $^{237}Np/^{239}Pu$ atom ratios

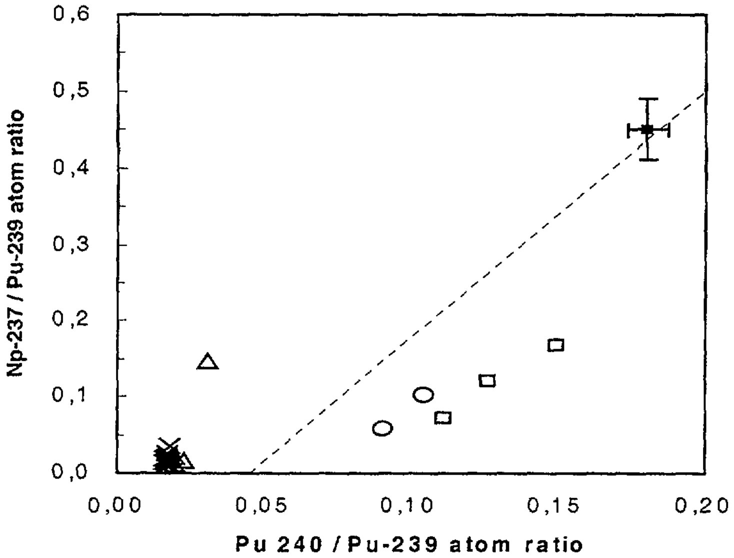

FIG. 6. $^{237}Np/^{239}Pu$ versus $^{240}Pu/^{239}Pu$ atom ratios in various Urals flod plain and river sediment samples.x: Nadirov Bridge (Fig. 4-5), Δ: Anchugova, Techa 170 km from Mayak, □: Ob River, O: Verkney Jahr, Iset River before confluence with Techa River. The line is Beasley et al.'s relation for northern hemisphere soils[10], and the single point indicate integrated fallout in Northern Tier Soils with 1σ errors[10].

average statistical error of the ICPMS ratio measurements, 0,0167 ± 0,0005 (SD, n=14).

For the ^{237}Np/^{239}Pu atom ratios (Fig. 5), the data indicates a peak at 20-26 cm. The significance of this excursion has not yet been verified by repeated measurements. It should be born in mind, that the ^{237}Np/^{239}Pu ratio is determined with a much higher uncertainty than the ^{240}Pu/^{239}Pu ratio because the amount of ^{237}Np is determined on the assumption of a predetermined average chemical yield and furthermore, the ^{237}Np/^{239}Pu ratio is based on two individual chemical separations and two ICPMS measurements, whereas the ^{240}Pu/^{239}Pu ratio is determined from one ICPMS run [1].

The ^{237}Np/^{239}Pu ratios from the Nadirov Bridge core (Fig. 5) are plotted as a function of the ^{240}Pu/^{239}Pu ratios in figure 6, together with other data from the Techa River, the Ob River, and the Iset

River. As compared with Beasley *et al.*'s [10] relation between the two atom ratios in Northern Hemisphere soils, shown as a line in Fig. 6, the Techa River samples show lower ^{240}Pu/^{239}Pu ratios. The Ob River and the Iset River data appears to have less ^{237}Np compared to the ^{240}Pu/^{239}Pu ratios. Different sources or differences in geochemical properties of neptunium and plutonium could cause this. However, bearing in mind the above remarks on uncertainty of the ^{237}Np/^{239}Pu ratios, the difference from Beasley *et al.*'s line is probably not significant on the present data except for the lower ^{240}Pu/^{239}Pu ratios in the Techa River sediments.

4. CONCLUSIONS

- Sediment samples from the Thule 1968 accident display significantly different ^{240}Pu/^{239}Pu atom ratios in the range 0.027 - 0.057. This supports the earlier conclusion [5] that the Thule plutonium originates from at least two sources of different quality, and that the Thule plutonium on average was "cleaner" than the plutonium lost at a similar accident in 1966 in Palomares, Spain [5].
- Significant correlations have been observed between ^{240}Pu/^{239}Pu atom ratios and ^{238}Pu/$^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu activity ratios in Thule sediment samples.
- The radioecological implication of the observed variations is that the use of plutonium isotope ratios in determining quantitatively the influence of different plutonium sources is a very complex affair requiring substantial data sets.
- The Nadirov Bridge sediments, Techa River, show lower ^{240}Pu/^{239}Pu atom ratios, 0,0167 ± 0,0005 (SD, n=14), than other contaminated sites reported by Beasley *et al* [10], and much lower than seen in debris from US nuclear weapons lost in Thule and Palomares.
- There is an indication that also the Iset River already before the confluence with the Techa River display isotope ratio signatures that are significantly different from global fallout (Fig. 6).
- Apart from the lower ^{240}Pu/^{239}Pu atom ratios in the Techa River, the presently observed relation between ^{237}Np/^{239}Pu and ^{240}Pu/^{239}Pu atom ratios in the Urals is in accordance with Beasley *et al.'s* observations [10].

Acknowledgements

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RADIOECOLOGICAL ASSESSMENT OF THE CONSEQUENCES OF CONTAMINATION OF ARCTIC WATERS - UPDATE ON THE PROGRESS OF THE EC-SUPPORTED ARMARA PROJECT

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Abstract

The potential radiological consequences of anthropogenic radionuclide contamination of the Arctic marine environmen has been assesed. To this end, model-directed sampling campaigns have been undertaken in the Arctic, and extensive data on radionuclide contamination and transfer mechanisms have been collected, interpreted and used to refine and validate an advanced compartmental model of radionuclide dispersal, with a view to predicting likely short- and long-term doses to man, and providing clear scientific guidelines for policy and decision makers should the need for remedial action or counter-measures arise in the future.

1. INTRODUCTION

The ARMARA project was initiated in late-1995 as a coordinated effort to address the issue of radioactive contamination of the Arctic environment in response to revelations about the disposal of large quantities of radioactive waste in the Barents and Kara Seas by the former Soviet Union. The project has a duration of three and a half years and is being carried out under the EC's Nuclear Fission Safety research and training initiative (Fourth Framework Programme, 1995-99). The collaboration comprises ten institutions from eight countries within the European Union (Denmark, Finland, France, Ireland, Italy, Spain, Sweden, United Kingdom) and a further three institutions from Norway (Fig. 1).

The overall objective of the project is to assess the potential radiological consequences of anthropogenic radionuclide contamination of the Arctic marine environment. To this end, model-directed sampling campaigns have been undertaken in the Arctic, and extensive data on radionuclide contamination and transfer mechanisms have been collected, interpreted and used to refine and validate an advanced compartmental model of radionuclide dispersal, with a view to predicting likely short- and long-term doses to man, and providing clear scientific guidelines for policy and decision makers should the need for remedial action or counter-measures arise in the future.

2. RESULTS

To facilitate the achievement of these objectives, the project was divided at the outset into ten distinct work programmes, each sub-divided into a set of relevant research activities. These work programmes sought to address the following: (i) scope of the current Arctic database, including existing models; (ii) design of model-directed sampling campaigns and experiments; (iii) short-term reactivity of radionuclides upon input into the Arctic and subsequent reactivity within the water column; (iv) reactivity at the fresh water/sea water interface and at the sediment/sea water interface; (v) fluxes, mixing layer processes and advective transport; (vi) transfer processes to living species, including man; and (vii) optimisation and validation of the RISØ-NRPA compartmental model for the Arctic (and the north-east Atlantic), and prediction of the likely dose consequences.

Thirty months into the project, substantial progress has been made on the key issues identified above [1]. A number of major collaborative expeditions have been undertaken in the high Arctic. Large quantities of data have been accumulated and environmental samples collected in the course of these expeditions, the analysis of which has yielded much new information on the behaviour of radionuclides under extreme conditions. These studies have been complemented by specific laboratory simulations and experiments carried out under controlled conditions, and have provided a set of realistic, site specific, parameter values for many of the processes controlling radionuclide dispersion and biological uptake in the Arctic. These parameter values have been incorporated into an advanced compartmental model which, in turn, has been used to predict past and future doses to individuals and critical groups on the basis of release scenarios as defined in the EC/DGXI Kara Sea project.

The model predicts that the collective dose (truncated at 10 000 years) to the world population will be in the order of 1 man-Sv. It also shows that the annual dose rate to individuals from a critical group located in the western Kara Sea peaked in the year 1970 at a value of 2×10^{-8} Sv y^{-1}, with ^{55}Fe contributing 99% of the dose. Further, the peak annual dose to individuals from this critical group in the year 3700 is predicted to be 2×10^{-9} Sv y^{-1} and is dominated by the plutonium isotopes.

Parameter sensitivity analysis shows that, for the total collective dose, the main sensitivities are due to sedimentation processes and biological transfer processes. All of these parameters have been measured repeatedly in the course of the present programme and remain the focus of attention, particularly in the context of site specificity.

In parallel with this, a refined version of the model has been developed which, while maintaining a box structure with uniform mixing in all boxes, also includes the dispersion of radionuclides over time Comparison of the calculations based on the more traditional approach with those obtained using the refined version shows that the latter gives a more realistic description of the dispersion of radionuclides within boxes. Preliminary results obtained with the new version of the model yield radionuclide concentrations which are up to an order of magnitude higher in the initial phase of dispersion than those obtained using traditional modelling Calculations of world collective doses to man indicate significant local differences (up to 30%) in comparison with the original model. However, it is interesting to note that the higher radionuclide concentrations in the initial phase of the dispersion obtained with the refined model do not necessarily translate into higher estimated doses.

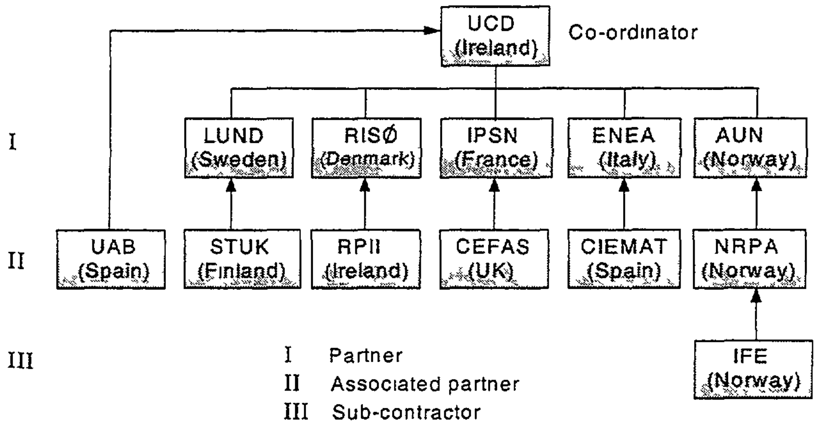

FIG. 1. Structure of the ARMARA collaboration

Acknowledgements

The support and encouragement provided by the European Commission's Services for this project is gratefully acknowledged (Contract F14P-CT95-0035)

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MARINE RADIOACTIVITY STUDIES IN THE WORLD OCEANS (MARS)

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Abstract

The International Atomic Energy Agency's Marine Environment Laboratory is carrying out from 1996 a project with international participation "Marine Radioactivity Studies in the World Oceans (MARS)". The main objectives of the project are to provide new data on marine radioactivity and to develop a better understanding of the present radionuclide distribution in the open ocean. Within the framework of the project, various research activities are being carried out to fulfill the objectives: Coordinated Research Programme (CRP), scientific expeditions to the open ocean, development of a database for marine radioactivity, evaluation of radionuclide distributions and dose assessments.

1. INTRODUCTION

There is a growing number of known sources of anthropogenic radioactivity in the marine environment. They include global nuclear fallout following atmospheric weapons tests, the Chernobyl accident, discharges of radionuclides from nuclear installations, dumping of radioactive wastes in the world's oceans and seas, nuclear submarine accidents, contributions from nuclear weapons tests sites, loss of nuclear weapons and radioactive sources, and satellite burn-up.

Due to variations in the source inputs and subsequent dispersion, mixing and transport of radionuclides in the world's oceans and seas, the marine environment is completely labeled with radionuclides differing from one region to another according to the predominant source in the region.

Assessment of marine radioactivity in a given region therefore requires knowledge of the source terms and an understanding of oceanic processes. The deposition of radioactivity from these sources is unevenly distributed over the world's oceans. The input function of global fallout in the world's oceans, mainly due to nuclear weapons tests carried out in the sixties, can be estimated from worldwide monitoring mainly performed on land. On the other hand, discharges from nuclear fuel reprocessing plants or dumping of liquid and solid radioactive wastes have generally had a more local character, but soluble radionuclides have been transported over long distances by prevailing currents.

In order to estimate radionuclide inputs from local sources, radionuclide distributions in the world's oceans and seas must be better known so that results from scientific expeditions to nuclear waste dumping sites and/or other sources of anthropogenic marine radioactivity can be reviewed objectively, comparatively and comprehensively. This requires a detailed study of the present distributions and inventories of the main radionuclides of interest (^{3}H, ^{14}C, ^{90}Sr, ^{137}Cs and Pu isotopes) in the world's oceans and seas as well as possible predictions of their concentrations for the near future.

As a contribution to these investigations, in 1996, the International Atomic Energy Agency's Marine Environment Laboratory (IAEA-MEL) commenced a five-year project "Marine Radioactivity Studies in the World Oceans (MARS)", with the generous support of the Science and Technology Agency (STA) of the Government of Japan.

2. OBJECTIVES OF THE PROJECT

The main objectives of the project are to provide new data on current radioactivity in the open ocean and to develop a better understanding of the present radionuclide distribution so that data sets obtained in national and international radioactivity surveys can be reviewed comparatively. The project also aims to contribute to scientific knowledge of the processes which affect radionuclide distribution and the sources which have introduced radioactivity to the open ocean.

The specific objectives of the programme are to:

i) examine present distributions of key radionuclides (^{3}H, ^{14}C, ^{90}Sr, ^{137}Cs and Pu isotopes) in water, sediment and biota of the world's oceans.

ii) extrapolate the results from contemporary ocean-wide surveys such as the tracer component of the WOCE where large sets of ^{3}H data are available and could be used for predictions of ^{90}Sr and ^{137}Cs concentrations in the same regions.

iii) study the development of radionuclide concentrations in water with time using good quality historical data (*e.g.* from the GEOSECS programme) with new data sets collected recently (*e.g.* from the IAEA '97 Pacific Ocean Expedition).

iv) identify the major sources of anthropogenic radionuclides in the world's oceans.

v) input all available data on radionuclide distributions in water, sediment and biota into the Global Marine Radioactivity Database (GLOMARD) so that temporal and spatial variations of key radionuclides can be investigated.

3. COORDINATED RESEARCH PROGRAMME

A Coordinated Research Programme (CRP) on "Worldwide Marine Radioactivity Studies (WOMORS)" was launched in 1998. Participants from Denmark, Germany, India, Italy, Japan, the Republic of Korea and the United States will contribute to the understanding of the present open ocean distributions of radionuclides in the water column and sediment and thus predict the radiological impact to be addressed. The CRP will encourage and support marine radioactivity studies in Member States by methodological assistance and total analytical quality management. The programme is designed to contribute to scientific knowledge of the processes which affect radionuclide distributions and the sources which have introduced radioactivity to the world's oceans. The CRP receives extrabudgetary support from the Government of Japan.

4. IAEA '97 PACIFIC OCEAN EXPEDITION

In accordance with the programme of the project, IAEA-MEL organized and/or participated in several scientific expeditions to the open ocean. The IAEA '97 Pacific Ocean Expedition was conducted in November 1997 in cooperation with 9 organizations from 5 Member States [1]. It was the first time in the history of the IAEA that an oceanographic expedition to the open ocean was fully organized and accomplished by the Agency.

The objective of the expedition was to sample water at various depths, to sample sediment cores and biota, and to perform oceanographic measurements (salinity, temperature, *etc.*) in the NW Pacific Ocean with the aim of investigating the distributions of anthropogenic and natural radionuclides in the marine environment (Fig.1). The analyses of collected samples and oceanographic measurements performed during the cruise will also help to study isotopic signals which may have been introduced by the "El Niño" effect. Further, these investigations will also look for possible latitudinal effects in the distribution of natural radionuclides in seawater, plankton and fish in the NW Pacific Ocean.

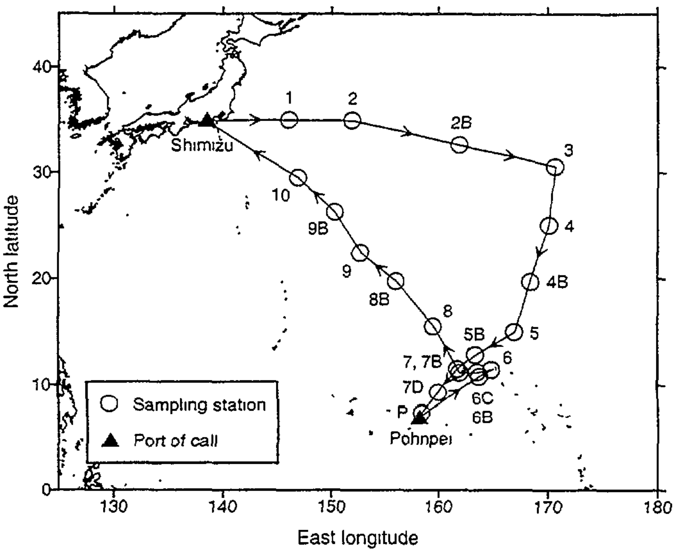

FIG. 1. Cruising chart and sampling stations for the IAEA '97 Pacific Ocean Expedition

Preliminary results obtained by CTD and general chemistry measurements performed during the expedition were presented in a cruise report [2] issued by IAEA-MEL soon after the expedition. The full analyses of collected samples will be carried out not only by IAEA-MEL and the participating organizations but also by other laboratories of Member States (Canada, Germany, India, Japan, New Zealand and the United States). The final results of all the analytical work will be published in 2000 in the form of an IAEA-TECDOC. Fig 2 shows an example of the analysis of collected samples for ^{3}H in water (measured by IGNS, New Zealand). Vertical profiles of ^{3}H concentrations are separated into two groups: one group has a large gradient of concentration up to 1000 m in depth and the other up to 500 m only. This grouping might depend on the depth to the bottom or the resultant depth of the mixing layer. Detailed discussion will be done later, using the bathymetric and oceanographic data.

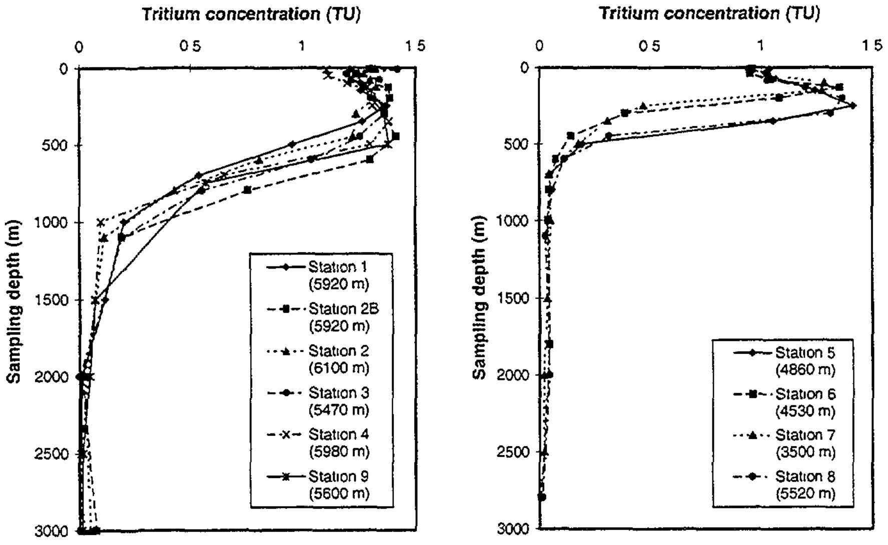

FIG. 2. Vertical profiles of ^{3}H concentrations in seawater obtained in the IAEA '97 Pacific Ocean Expedition

5. JAPANESE-KOREAN-RUSSIAN JOINT EXPEDITIONS TO THE NW PACIFIC OCEAN AND ITS MARGINAL SEAS

Within the framework of a joint agreement between the Governments of Japan, the Republic of Korea and the Russian Federation, IAEA-MEL was invited to participate in the Japanese-Korean-Russian joint expeditions to radioactive waste dumping areas in the NW Pacific Ocean and its marginal seas [3, 7]. The primary objective of the expeditions was to investigate the radiological contamination of the marine environment due to radioactive wastes dumped in the past by the former USSR, the Russian Federation, the Republic of Korea and Japan. The expedition was carried out on board a Russian research vessel '*Okean*' in 2 stages: the first in March/April 1994, visiting dumpsites in the Sea of Japan/East Sea, and the second in August/September 1995, visiting dumpsites in the Sea of Okhotsk, the NW Pacific Ocean and the Sea of Japan/East Sea.

Seawater from surface and bottom waters and seabed sediments were sampled at 14 stations in the areas where radioactive wastes of more than 700 TBq had been dumped and at additional 6 stations outside these areas, the latter reflecting background levels. In 2 areas where larger amounts of radioactive wastes had been dumped, intermediate water was also collected at several depths. In addition, sampling work was done at 2 stations in an area close to Sakhalin Island in the Sea of Okhotsk where a ^{90}Sr source of 13 PBq was accidentally lost. Surface water was collected with a pumping system, and the bottom and intermediate waters with a LVS. Sediment sampling was carried out using a grab sampler. Biota (zooplankton and benthos) were also sampled at each station.

The analytical results showed [5, 7] that the concentrations of ^{3}H, ^{90}Sr, ^{137}Cs, ^{238}Pu and ^{239,240}Pu in seawater and sediment of the dumping areas were low and not significantly different from those found in corresponding background areas. The levels also compared well with those generally found in the NW Pacific Ocean and its marginal seas. The estimated total inventories of ^{90}Sr, ^{137}Cs and ^{239,240}Pu in water and sediments were also consistent with previous observations in these regions. Results of radionuclide inventories and isotopic activity ratios (^{137}Cs/^{90}Sr, ^{239,240}Pu/^{90}Sr, ^{239,240}Pu/^{137}Cs and ^{238}Pu/^{239,240}Pu) supported the conclusion of the predominance of global fallout at the sampling areas.

6. FURTHER EXPEDITIONS

Further expeditions carried out in 1997-1998 or planned for 1999 are:

- Indian Ocean; March-April 1998, '*Italica*', in co-operation with the National Agency for New Technology, Energy and Environment (ENEA), Italy.
- North Indian Ocean (the Arabian Sea); March-April 1998, '*Sagar Sampada*', in co-operation with the Physical Research Laboratory, India.
- Atlantic Ocean; August – September 1998, *"Walter Herwig"*, in co-operation with the Federal Fisheries Research Centre, Germany.
- South Indian Ocean; January-February 1999, *" Marion Dufresne"* in co-operation with CNES, France.

7. DEVELOPMENT OF A DATABASE FOR MARINE RADIOACTIVITY

In the framework of the project, IAEA-MEL has developed the GLOMARD [8] (Global Marine Radioactivity Database) to provide Member States with data on radionuclide concentrations in the marine environment. This information will help Member States in radiological assessments related to radioactive waste dumping and nuclear bomb testing, and in emergency response to radiological accidents at sea. It is planned to make the GLOMARD available in the near future on the 'Internet' or the 'IAEA-MEL Website'. The GLOMARD contains approximately 40 megabytes of data, representing 100,000 measurements of radioactivity in seawater, sediment, biota and suspended matter sampled from the world's oceans.

The current version of the GLOMARD allows the inputting, maintenance and extraction of data for the production of various kinds of maps using external programs, *e.g.* 'Surfer', 'Mapinfo', *etc.* Extracted data are processed by these external programs to produce contoured maps representing radionuclide distributions in studied areas. The new version of the GLOMARD will be connected to the GIS which will allow the production of more precise 2D and 3D maps where radioactivity data will be correlated with data on bathymetry, temperature or salinity. It will also be possible to produce time-series contamination maps.

8. DISTRIBUTIONS OF RADIONUCLIDES IN THE NW PACIFIC OCEAN

As an example, the distributions of radionuclides in surface seawater and surface layer sediment of the NW Pacific Ocean were investigated using data sets installed in the GLOMARD. The data are from Japanese institutions, mainly from the Japan Chemical Analysis Center (JCAC). Evaluation of data was carried out for the vertical profiles of radionuclide concentrations, radionuclide inventories and their isotopic activity ratios in both seawater columns and sediment cores.

Generally the concentrations of ^{90}Sr, ^{137}Cs and ^{239,240}Pu in marine samples collected around Japan are very low and show a tendency to decrease year by year. The profiles of ^{90}Sr and ^{137}Cs in seawater columns show a gradual decrease in concentration with increasing depth, contrasting with those of ^{239,240}Pu which show a subsurface maximum at around 700 m depth, reflecting specific scavenging processes in the water column. The concentrations of radionuclides in sediment cores tend to decrease with increasing depth. The inventories of ^{90}Sr, ^{137}Cs and ^{239,240}Pu in seawater and sediment were estimated for several periods since the beginning of the eighties up to the present. Isotopic activity ratios in sediment cores are quite different from those in the seawater columns, reflecting the difference in the removal of radionuclides from seawater to the bottom sediment.

Fig.3 show a comparison of the ^{90}Sr inventories in the seawater column obtained in the Japanese-Korean-Russian joint expeditions with those in the past. The inventories of ^{90}Sr, ^{137}Cs and ^{239,240}Pu in the dumping area in the Sea of Japan/East Sea are 3.0, 5.8 and 0.10 kBq/m^2, respectively. In comparison, ^{90}Sr, ^{137}Cs and ^{239,240}Pu inventories in the dumping area in the NW Pacific Ocean are 1.0, 1.9 and 0.053 kBq/m^2, respectively. The inventories in water at the Sea of Japan dumping area are significantly higher than those in the NW Pacific Ocean. The inventories in the dumping areas, however, compare well with previous observations in the region. The total inventories in water and sediments observed in the Sea of Japan and subtropical Pacific Ocean show a surplus, compared with expected global fallout deposition densities. The surplus could be partly explained by the geophysical

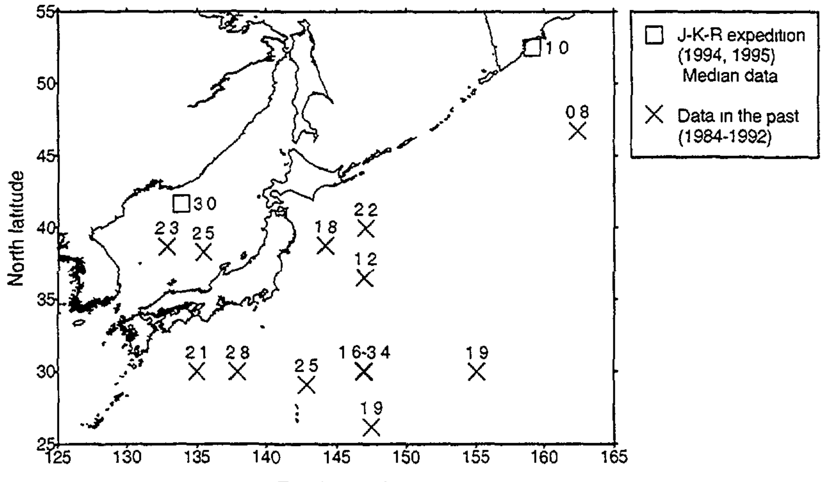

FIG. 3. Inventories of ^{90}Sr in the seawater column (kBq/m^2) in the NW Pacific Ocean and its marginal seas

processes occurring in the Sea of Japan [5, 6] and additional input from close-in fallout transported from the Central Pacific Ocean.

As a result of surveys in the Sea of Japan and the NW Pacific Ocean, there is no definitive evidence of the effect of radioactive waste dumping, although unique oceanographic features in the behavior of radionuclides have been found.

9. CONCLUSIONS

The sources which have introduced radionuclides into the world's oceans and seas, the distributions of anthropogenic and natural radionuclides in the marine environment (seawater, sediment and biota) and the contribution of anthropogenic and natural radionuclides to doses to the world population from marine radioactivity through ingestion of sea foods will be further investigated. The discussions will help to clarify the contributions from global nuclear fallout, discharges from nuclear industry, from former nuclear bomb testing at sites in the North and South Pacific Ocean, from former radioactive waste dumping sites (NE Atlantic, Arctic and NW Pacific Oceans) and from the Chernobyl accident to the total radioactivity observed in oceans and seas.

Acknowledgement

We are grateful to the Science and Technology Agency of Japan for support as well as to all participating institutions in the project. IAEA-MEL operates under a bilateral agreement between IAEA and the Government of Monaco.

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THE GLOBAL OCEAN OBSERVING SYSTEM (GOOS): NEW DEVELOPMENTS

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Abstract

GOOS will provide information about the present and future states of seas and oceans and their living resources, and on the role of the oceans in climate change. Among other things, it will include monitoring the extent to which the sea is polluted, and applying models enabling the behaviour of polluted environments to be forecast given a variety of forcing conditions including anthropogenic and natural changes. Implementation has begun through integration of previously separate existing observing systems into a GOOS Initial Observing System, and through the development of Pilot Projects, most notably in the coastal seas of Europe and North-east Asia. Although the present emphasis is on the measurement of physical properties, plans are underway for increasing the observation of chemical and biological parameters. The main biological thrust at present comes through the Global Coral Reef Monitoring Network (GCRMN). Consideration needs to be given to incorporation into the GOOS Initial Observing System of present national, international and global chemical and biological monitoring systems, and the development and implementation of new chemical and biological monitoring subsystems, especially in coastal seas for monitoring the health of those environments. GOOS will offer marine scientists and other users a scheme of continuing measurements on a scale larger in time and space than can be accomplished by individuals for their own applications, and a vastly improved store of basic marine environmental data for a multitude of purposes. For GOOS news see the GOOS Homepage at http://ioc.unesco.org/GOOS/.

1. INTRODUCTION

The vision guiding the development of GOOS is one of a world where the information needed by governments, industry, science and the public to deal with marine related issues, including the effects of the ocean on climate, is supported by a unified global network that will systematically acquire, integrate and distribute ocean observations, and generate analyses, forecasts and other useful products [1,2]. In response to this vision, GOOS will provide information about the present and future states of seas and oceans and their living resources, and on the role of the oceans in climate change. It will include monitoring the extent to which the sea is polluted, and applying models enabling the behaviour of polluted environments to be forecast given a variety of forcing conditions including anthropogenic and natural changes [3, 4, 5, 6].

2. THE COASTAL DIMENSION

A global observing system is clearly needed to monitor climate change and the effects of pollution by excess greenhouse gases. But why have a global observing system for coastal problems, like those caused by runoff from land? While coastal seas and their ecosystems are not in themselves global, the achievement of a predictive understanding of coastal ecosystems depends on the development of regional to global networks that link observation and analysis in more effective and timely ways [2, 7]. GOOS is thus promoting integration of the fragmented coastal environmental research community and its linkage to the community at large, especially user groups like policy makers, environmental and resource managers, Non-Governmental Organisations (NGOs), the business community, and the public in general, to enable them to get the scientific information they need to make informed decisions in a timely fashion.

GOOS is also promoting a broad-scale view of coastal ecosystems that takes into account the large scale forcing of the coastal system and which leads to reliable mechanisms for predicting environmental changes and their ecological consequences. The ultimate goal of the coastal GOOS program is to encourage and support the development and application of now-casting, forecasting and predictive capabilities as a means of preserving healthy coastal environments, promoting sustainable uses of coastal resources, mitigating coastal hazards, and ensuring safe and efficient marine operations [7].

In another sense, we need a global observing system, even for monitoring pollution, because ocean processes know no national boundaries and the ubiquitous nature of many of the problems to be solved means that it is often prudent to implement even local and regional operational or research programmes co-operatively and in a co-ordinated way. Such co-ordination needs to be carried out so as to achieve economy of scale and mutual support, and to enable future global extension.

Fifty percent of the world's population lives within 200 km of the coast, and 2/3 within 400 km [8]. The proportion is increasing, and over the next 50 years perhaps 2/3 of the world's population will live within 200 km of sea coasts and estuaries. Expected absolute and relative growth in coastal population, with the attendant pressure on natural resources, suggests that the pressure on the coastal environment will increase in pace with demands for its (preferably sustainable) use. Wetland and other shoreline areas are extremely important breeding and spawning areas for many species of fish and other organisms and yet, globally, over 50% of such areas have already undergone severe environmental degradation. Safe and efficient management of the marine environment under such conditions demands an increase in information about it, of the kind that can only be provided satisfactorily by a carefully designed monitoring system integrating various disciplines (physics, chemistry biology, geology) and data streams (ships, floats, buoys, aircraft, submersibles, radar's, satellites). To meet this requirement the United Nations Conference on Environment and Development in Rio in 1992 called in its Agenda for the 21st Century (Agenda 21) for creation of a Global Ocean Observing System (GOOS).

3. BENEFITS AND BENEFICIARIES

Calculations of costs and benefits suggest that the implementation of GOOS is likely to repay investment at a ratio of 10:1 or more [2, 9]. Beneficiaries of GOOS products will include managers and users of coastal defences, ports and harbours, fishing and fish farming, shipping, offshore industry, waste disposal and recreation, as well as Governments seeking to implement Agenda 21; the Global Plan of Action for the Protection of the Marine Environment from Land-Based Activities; and related instruments [2, 9, 10]. GOOS will offer marine scientists and other users a scheme of continuing measurements on a scale larger in time and space than can be accomplished by individuals for their own applications, and a vastly improved store of basic marine environmental data for a multitude of purposes [11].

4. IMPLEMENTATION

Implementation of GOOS, which is sponsored by the IOC, the WMO (World Meteorological Organisation), UNEP (United Nations Environment Program), and ICSU (International Council for Science) has begun, based on the integration of previously separate existing observing systems, and the development of Pilot Projects [2]. GOOS will develop to full global scale over the next 10-15 years as new monitoring systems are integrated into it, including the chemical and biological ones pertaining to the management of sustainable healthy coasts [7].

4.1 The GOOS Initial Observing System

The GOOS Initial Observing System integrates earlier observing systems [2]. It currently includes mostly open ocean physical observations in support of climate studies, which also provide data about the forcing of coastal seas. It includes some coastal elements, such as the tide gauge data from the Global Sea

Level Observing System (GLOSS), and the Global Coral Reef Monitoring Network (GCRMN). Other elements are:

- upper ocean measurements of the Ship of Opportunity Programme (SOOP)
- meteorological observations of the Voluntary Observing Ship programme (VOS)
- data from the fixed and drifting buoys of the Data Buoy Cooperation Panel (DBCP)
- data from the buoys of the Tropical Atmosphere Ocean (TAO) array set up to monitor El Niño
- data from the Global Temperature and Salinity Profile Programme (GTSPP)
- marine meteorological and ocean data from NOAA operational satellites
- communication through the Global Telecommunication System (GTS) of WMO.

These elements of GOOS are already of proven value to the communities that started and support them. For instance, there is no disputing the value of El Niño forecasts based on data collected by the TAO array.

4.2 GOOS Regional Pilot Projects

Most of the Pilot Projects developed so far are centred on the coastal seas of Europe (the EuroGOOS Pilot Project [12]) and North-east Asia (the NEAR-GOOS Pilot Project [13]). Initially they too focus on the physical data, not least because those data happen to be the most abundant and there is a well developed user community requiring them. However, chemical (nutrient) and biological (plankton) parameters also feature prominently in the EuroGOOS programme, and NEAR-GOOS is now moving to embrace such parameters. The initial focus in these and other Pilot Projects tends to be on data exchange, with a move eventually towards development of a numerical modelling and forecasting capability. Different Projects are moving in this direction at different rates.

Other Pilot Projects are now being developed in the Mediterranean Sea (MedGOOS)[14] and the Pacific islands (PacficGOOS)[15].

4.3 The Future

GOOS organisers recognise that more effort now has to be put into developing monitoring systems covering chemical and biological information and their integration with physical data [1, 2, 3, 6, 7]. This is especially true for coastal seas where most living marine resources exist. The monitoring requirements for these environments are now actively being considered by three GOOS Advisory Panels: (i) the Coastal GOOS (C-GOOS) Panel; (ii) the Health of the Oceans (HOTO) Panel, which is concerned with contamination and pollution of coastal seas and with marine responses to anthropogenic inputs; and (iii) the Living Marine Resources (LMR) Panel, taking into consideration the needs of resource managers and other users.

Examples of existing global biological and chemical observing systems currently under consideration for inclusion in the GOOS Initial Observing System include the Harmful Algal Bloom (HAB) programme of the IOC; the international Mussel Watch program; the Marine Pollution and Monitoring Program (MARPOLMON); and the Continuous Plankton Recorder (CPR) programme.

In due course, GOOS will incorporate not only existing international monitoring systems but also existing national monitoring systems provided they agree with the published GOOS Principles [1].

The (HOTO) Panel is developing plans for pollution-related Pilot Projects in marginal seas that appear to be most at risk, including east Asian seas, the Black Sea, the Red Sea and the Arctic [6]. Together with C-GOOS, the HOTO Panel will also be considering the development of Pilot Projects in the Adriatic and Caribbean. The HOTO-driven Pilot Projects will be developed in the context of a Strategic Plan that has been drafted for pollution monitoring within GOOS [3,4,5].

The HOTO Panel is also beginning to consider (i) how to develop indicators of the sustainability of marine environments, as a guide to coastal seas management, and (ii) the development of numerical models to aid in forecasting, to assist in assessing the sustainable development of ecosystems [6].

Forecasting using sophisticated physical-biogeochemical ecosystem models that incorporate living and non-living components of the system may prove useful, for instance, as the basis for a variety of early warning systems, eg for eutrophication (which may lead to increased algal blooms, anoxia, massive fish deaths and major alterations in biological communities). Simpler models coupled with dynamic models of regional circulation can be used to predict the dispersion of passive tracers such as oil spills, and accidental releases of contaminants, radioactive tracers and sediment load. Water quality modelling can assist in the development and possibly predict the effectiveness of measures to prevent pollution and contamination in the water column. Numerical models may also add value to data by enabling interpolation between data points, and enabling estimation of some of model parameters from a limited number of observations under certain constraints, thereby complementing data obtained by the HOTO observing system.

The list of variables that could be monitored under the HOTO Strategic Plan includes: (i) physical measurements (solid litter and plastic; and suspended particulate matter; (ii) chemical measurements (synthetic organics; polycyclic aromatic hydrocarbons; trace metals; petroleum (oil); herbicides and pesticides; dissolved oxygen; artificial radionuclides; and pharmaceuticals); and (iii) biological measurements (phytoplankton pigments and community structure; human pathogens; nutrients; and algal toxins), which can be used to provide indications of biological distress that may be useful in determining the sustainability or otherwise of marine ecosystems [3,4,5,6]. However, what is actually measured in any one region under the HOTO programme will depend on the design of the monitoring programme and will flow from its goals and objectives.

Aside from the design of different facets of the observing system, GOOS organisers are also involved in formulating plans for a data and information management system and service [2]. Initially, by default, it comprises the data and information management components of the elements of the GOOS Initial Observing System and of the GOOS Pilot Projects.

5. TRAINING AND CAPACITY BUILDING

For GOOS to be fully global demands that all coastal countries are able to contribute to and benefit from it. For its realisation, this dream requires a considerable rise in the capabilities of many developing countries so that at the very least they can gather, process and interpret data, exchange data with neighbours and other GOOS partners, and provide products valued by the local or regional user community. This requires; (i) the building of appropriate institutional infrastructure, (ii) the training of more scientists to appropriate levels, and (iii) provision of or access to appropriate equipment [1, 2]. Developed nations and aid agencies will need to take these requirements on board if they are to obtain the benefits of a fully global GOOS.

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"MUSSEL WATCH"AND CHEMICAL CONTAMINATION OF THE COASTS BY POLYCYCLIC AROMATIC HYDROCARBONS*

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Abstract

Polycyclic aromatic hydrocarbons (PAH) enter the coastal marine environment from three general categories of sources; pyrogenic, petrogenic (or petroleum), and natural diagenesis.

PAH from different sources appear to have differential biological availability related to how the PAH are sorbed, trapped, or chemically bound to particulate matter, including soot. Experience to date with bivalve sentinel organism, or "Mussel Watch", monitoring programs indicates that these programs can provide a reasonable general assessment of the status and trends of biologically available PAH in coastal ecosystems. As fossil fuel use increases in developing countries, it is important that programs such as the International Mussel Watch Program provide assessments of the status and trends of PAH contamination of coastal ecosystems of these countries.

1. INTRODUCTION

Modern societies have deliberately and inadvertently discharged or released chemicals of environmental concern to the coastal ocean for decades. The serious nature of several of the ensuing problems identified in the 1960s and early 1970s demonstrated the need for an organized and systematic approach to assessing the status and trends of contamination of coastal and estuarine ecosystems by selected chemicals of major concern. Surveys in the 1960s and early 1970s involving sampling and analysis of various components of coastal and estuarine ecosystems led to the conclusion that much could be learned about spatial and temporal trends by sampling and analyzing carefully chosen populations of bivalves. Writing in 1975, Professor Edward D. Goldberg of Scripps Institution of Oceanography, California, USA [1] called for a "Mussel Watch" Program of assessment of contamination of the world's coastal oceans by using the bivalve sentinel organism approach for monitoring of selected chemicals. Shortly thereafter a few national or regional programs, for example the U. S. EPA "Mussel Watch" Program, were implemented as prototype monitoring programs. Valuable, multi-year experience was gained with this type of approach to coastal and estuarine monitoring and several important lessons were learned in these efforts, including the need for very close coupling of the monitoring program with ongoing biogeochemical and biological/ecological effects research [2-13].

A special concern for coastal areas of developing countries led to the establishment of the International Mussel Watch Program to provide an initial survey of coastal areas of developing countries for selected chemical contaminants, initially chlorinated pesticides and chlorobiphenyls, and to provide a framework for operational monitoring programs in individual countries and regions [5,7-10]. I submit that progress has been slower than originally anticipated and a global survey within a few year period of time has not been achieved to date as originally envisioned [8-10]. My personal experience suggests that this is the result of higher priorities being assigned elsewhere within international environmental quality efforts and a scarcity of funding to meet all the needs for research and monitoring for global environmental concerns.

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Chlorinated pesticides and chlorobiphenyls were the chemicals chosen for the focus during the initial stages of the International Mussel Watch Program. There was continuing use of chlorinated pesticides in some developing countries and data for both chlorinated pesticides and chlorobiphenyls could be obtained with modest additional analytical effort because of similarities in chemical properties of the compounds [5,8-10]. I contend in this paper that there are significant reasons for using the International Mussel Watch approach to assess the status and trends of concentrations of bioavailable polycyclic aromatic hydrocarbons in coastal areas in addition to chlorinated pesticides and chlorobiphenyls. A brief review of our knowledge of PAH biogeochemistry in coastal ecosystems followed by a summary from the ongoing US NOAA Status and Trends Mussel Watch Program and result from Phase I of the International Mussel Watch Program are presented in support of this contention.

2. BIOGEOCHEMISTRY OF POLYCYLIC AROMATIC HYDROCARBONS: SEDIMENTS AND BIVALVES

Polycyclic aromatic hydrocarbons (PAH) are among the chemicals of environmental concern for three main reasons. First, some of the individual PAH are protocarcinogens, that is uptake by organisms and biochemical activation to carcinogens is of significant potential under some conditions found in nature [14,15]. Second, other PAH can have deleterious effects on marine organisms if taken up by these organisms to high concentration levels [16]. Third, modern human civilization's activities are mobilizing these compounds to enter the environment, including the coastal environment, at rates much higher than natural rates before modern civilization [14,17-20].

Major sources of PAH input to the environment are listed in table I. It is important to keep in mind that there are hundreds to thousands of individual PAH structures in some of the sources of inputs. Despite significant analytical chemistry progress in analysis of PAH during the past three decades, there are formidable challenges remaining for analyses of environmental burdens of PAH. The details of that story are not the subject of this paper, but analyses of PAH in environmental matrices should be recognized as a continuing analytical chemistry challenge. During the mid-1970s when PAH data were collected for sediments from coastal areas, parameters were noted that distinguished in a general way between pyrogenic (parent PAH predominated over alkylated PAH in a homologous series) and petrogenic sources (alkylated PAH predominated over the parent PAH in a homologous series)[17,18]. The PAH composition of sediments generally indicated a pyrogenic origin from either, or both, natural fires and combustion of fuels by human activities [17,18}. PAH with a petrogenic source composition were found only in the most heavily industrialized harbor sediments or at oil spill sites, and often they were mixed with PAH with a pyrogenic source composition [17,18]. This has been confirmed several times during the past fifteen years [14,19,20]]. Use of ratios of selected isomer pairs sometimes discriminates further between combustion sources [21,22]. More recently, the ratios of stable isotopes of carbon and radioactive carbon content of individual PAH have been added as powerful parameters available for apportioning sources of the mixture of PAH present in various types of samples [23,24].

TABLE I. MAJOR SOURCES OF PAH INPUTS TO THE ENVIRONMENT.

Pyrogenic Input.	Petroleum
Combustion of Fossil Fuels.	Oil seeps, Oil Spills, Chronic Oil releases
Transportation.	
Exhaust, Used lubricating oil	
Home heating and cooking	Automobile and Truck Tires
Electric power generation	
Industrial uses.	Early Diagenesis of Organic Matter
Forest and Grass Fires	
Home cooking and heating using wood, dung	
Creosote, Tar, Asphalt	

Samples of mussels or oysters were collected at approximately 100 stations around the U. S. between 1976 and 1978 as part of the USEPA funded "Mussel Watch" [2-4], a prototype for the current US NOAA Status and Trends Program [25]. Bivalves from approximately fifty sites in the USEPA "Mussel Watch " Program were analyzed for PAH by quantitative GCMS by our group in Woods Hole. Bivalves sampled near urban harbor sites, for example New York and Boston, had elevated concentrations compared to samples from more remote locations such as the coast of Maine [4,26]. This was not a major surprise given the data for elevated PAH in sediments sampled near urban harbor areas [17-20]. The surprise came in the way of the qualitative mixture of PAH present; more petrogenic in origin than the PAH mixture found in sediments [4,26]. Bivalves in more remote locations with lower concentrations had primarily a pyrogenic source signature in accord with sediment PAH in remote locations [4,26]. We hypothesized that the pyrogenic PAH were more tightly bound to particles from combustion processes and thus were less bioavailable than petrogenic PAH which enter the coastal environment in various forms and were less tightly bound to particles and also dissolved or accommodated in water [4,26]. This highlighted the need to improve our understanding of the physical chemistry of the PAH in the environment and to understand how this relates to bioavailability of PAH.

At about the same time as our research led us to this hypothesis, Readman, Mantoura and others in Plymouth at the U. K. were researching and publishing results about PAH biogeochemistry of PAH in the Tamar Estuary, U. K. [27]. Their results, those of Prahl and Carpenter [28], Socha and Carpenter [29], Broman and co-workers [30], and more recent Ph. D. thesis research results of Susan McGroddy [31,32] Keith Maruya [33,34] Christopher Reddy [35] and Orjan Gustaffson [36,37], among several other research efforts, have contributed substantially to our present understanding of the physical-chemical form of PAH and relationships to bioavailability. Figure 1 is a simplified cartoon view of major physical chemical forms of PAH. The importance of binding to soot (bottom right example in figure 1.) has been discussed in theoretical terms and used to explain aspects of field observations of pore water-particle partitioning in sediments [36,37].

This improved understanding of the biogeochemistry of PAH in coastal ecosystems informs, or should inform, policies for regulating and reducing inputs of PAH, and to guide restoration and cleanup efforts in some heavily contaminated areas. Use of fossil fuels in developed countries continues to increase, albeit slower than before, as indicated by assessments and estimates of carbon emissions [38]). There are policies in place, such as recycling used motor oil, which should result in reduced release to the environment of amounts of PAH/unit fuel used. Have these policies been effective in reducing environmental burdens of PAH? What is the status of bioavailable PAH concentrations in coastal ecosystems?

3. PAH IN COASTAL ECOSYSTEMS: PRESENT AND FUTURE STATUS AND TRENDS

The U.S. NOAA Status and Trends Program provides high quality monitoring data that yields a portion of the answer for the U. S. Coast. Bivalves from over 100 sites have been sampled and analyzed annually between 1986 and 1995 for the suite of PAH [25,39]. Concentrations of PAH in bivalves have about the same distribution that we noted in our prototype efforts of the late 1970s; elevated concentrations are found near urban harbor areas and lower concentrations are found in remote locations [25,39]. The main issue relevant to this presentation is the temporal trend. A summary of the observed temporal trends for organic chemicals of environmental concern analyzed in the program is presented in table II [39]. For PAH, three sites had trends of increasing concentration, three sites had trends of decreasing concentrations and for the remaining 180 sites the concentrations remained the same. This contrasts with several other suites of organic chemicals of environmental concern for which at most only one site had an increasing trend and many more sites had decreasing trends (Table II). There is good news in these data since the continued increased use of fossil fuels has not resulted in trends of increasing concentrations of PAH. For urban harbor areas with high concentrations of PAH in bivalve tissues, the continued elevated concentrations may be sustained by inputs to the surrounding ecosystem from sediments containing past inputs of PAH. [31-34].

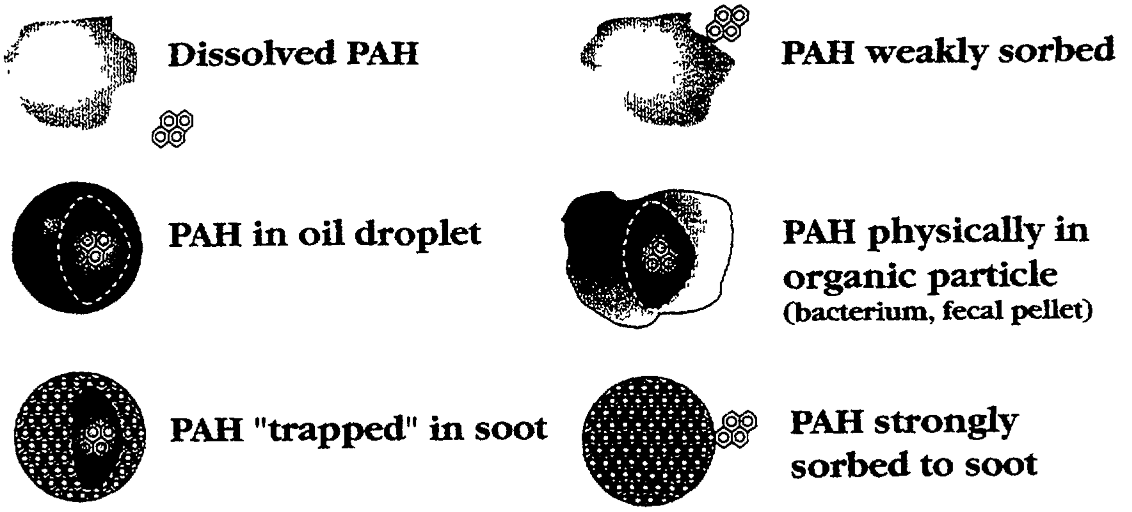

FIG. 1. Some Physical-Chemical Forms of PAH in the Environment: Example of Pyrene Interaction with Particulate Organic Matter, Oil Droplet and Soot. Modified from Reference [27].

TABLE II. U. S. NOAA STATUS AND TRENDS MUSSEL WATCH DATA: NUMBERS OF SITES WITH INCREASING, DECREASING, OR NO TREND IN CONCENTRATIONS OF EACH CHEMICAL. 1986-1995[39].

Chemical	Increase	Decrease	No Trend
*ΣChlordane	1	81	104
*ΣDDT	1	38	147
*ΣDieldrin	1	32	153
*ΣPCB	1	37	148
ΣPAH	3	3	180
*ΣButyl Tins	0	18	168

*Chemicals with decreasing trends in concentrations in mussels and oysters.

These data and interpretations for the U. S. coast are of concern when combined with limited data available for PAH in samples from coastal areas of developing countries. During the first phase of International Mussel Watch in the Central, South America, and Caribbean regions, the emphasis was on analyses of chlorinated pesticides and selected PCB congeners [8, 40]. In addition, Sericano et al [40] analyzed many of the samples for the same suite of PAH analyzed for the NOAA Status and Trends Program. The range of concentrations of PAH are similar to those found in the U. S. National Status and Trends Program, with fewer samples of the total having elevated concentrations. Elevated concentrations are found near urban areas, and the composition of the PAH indicate a mixture of petrogenic and pyrogenic sources [40].

These measurements are one point-in-time - a survey. A good start, but insufficient if we consider the known and projected fossil fuel use indicated by carbon emissions trends for developing countries [38]. This will lead to an increase in by-product combustion source PAH and there will be increased mobilization of petroleum PAH. Leakage will occur and it is likely that environmental burdens of PAH will increase in coastal areas. The extent of the increase will depend upon how lessons from the developed countries about curtailing sloppy use of fossil fuels and reducing inputs of PAH are adopted and adapted to policy and management decisions in developing countries.

I am concerned that there are no systematic collections of PAH data for coastal areas that will provide assessments of trends over time and space, and provide feedback for effective management of the inputs of PAH to coastal ecosystems in developing countries. The International Mussel Watch Program and follow-on or associated regional programs offer a means to track trends in bioavailable

PAH concentrations. I do not advocate a focus on PAH to the exclusion of other chemicals of environmental concern. Coupled with emerging and powerful biological effects measurements, assessments of the status and trends of coastal ecosystem burdens of chemicals of environmental concern can provide for a powerful monitoring methodology that should be applied in coastal areas worldwide.

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GLOBAL ASSESSMENTS OF THE STATE OF THE MARINE ENVIRONMENT: CONTEMPORARY INITIATIVES

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Abstract

A large number of assessments of regional marine areas have been conducted in recent years for a variety of purposes. Periodic reviews of the state of the marine environment have been undertaken by the United Nations Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP[1]). The most recent of these global assessments was published in 1990. The international adoption of a Global Programme of Action for the Protection of the Marine Environment from Land-Based Activities in 1995 has led to additional demand for regional assessments and a global review. The regional assessments are either completed or in train largely through mechanisms associated with the UNEP Regional Seas Programme. The global assessment has been assigned to GESAMP and incorporated into its plans for the preparation of a new global review to be completed in the year 2002. The Intergovernmental Oceanographic Commission, (IOC) the Scientific Committee for Oceanic Research (SCOR) and the Scientific Committee on Problems of the Environment (SCOPE) are collaborating in a review of ocean science. The Global Environment Facility (GEF) recently approved funding for a "Global International Waters Assessment" (GIWA) partly as a means of determining priorities within its International Waters Portfolio. This paper outlines the nature of, and contemporary activities within, these various assessments.

1. INTRODUCTION

A marine environmental assessment is a process by which information is collected and evaluated, and undertaken periodically to assess the state of knowledge regarding a specific marine area. It provides a mechanism for summarizing existing information that can be used to form opinions about the "*quality*" of the environment concerned. The benefits offered by assessments of marine environmental conditions have been recognized since the early 1970s. They have led to sustained effort within the framework of the Helsinki Commission for the Baltic Sea and the Oslo and Paris Commission for the northeast Atlantic to prepare periodic reviews of the state of their respective jurisdictional areas. Assessments have also frequently been explicit components of new regional marine agreements including those formulated under the Regional Seas Programme of the United Nations Environment Programme (UNEP). Indeed, the use of such assessments to identify and set priorities for management intervention in favour of the protection of the marine environment, its resources and amenities, has been the primary purpose for their preparation. Nevertheless, these assessments offer other benefits. The overall purposes of marine environmental assessments has been as outlined by GESAMP [1] as follows:

- providing a compact summary of contemporary knowledge, status and trends in environmental quality and necessary management action;
- enabling the identification of significant gaps in knowledge and, accordingly, providing an authoritative basis for defining priorities for further scientific and other investigations; and

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[1] Prior to 1983 the acronym GESAMP stood for the United Nations Joint Group of Experts on the Scientific Aspects of Marine Pollution

- providing a basis for judging the effectiveness and adequacy of environmental protection measures and for making any necessary adjustments to these measures.

2. REGIONAL ASSESSMENTS

There have been a plethora of regional assessments conducted in the last three decades. Examples are those for the Caribbean Sea [2, 3, 4, 5], the Mediterranean Sea [6, 7, 8], the Black Sea [9], East Asian Seas [10] and the Arctic [11, 12]. These are in addition to assessments of specific topics within these and other areas such as the effects of climate change, atmospheric inputs of substances and the condition of mangroves and corals [*e.g.*, 13, 14, 15, 16]. Notable among these have been periodic assessments prepared within the Baltic Sea community under the aegis of the Helsinki Commission [17, 18] and those prepared on the North Sea in conjunction with the Oslo and Paris Commissions [19, 20]. Although these two areas have been the subjects of the highest frequency of assessments, it would be wrong to conclude that they are the most informative. Assessments of information on other areas, such as the Mediterranean and the Black Seas, have now been refined to the point that they are yielding extremely valuable guidance to the riparian states. This is largely because they focus on the assessment of effects rather than the mere evaluation of conditions such as the levels and sources of contaminants. Such is not the case for the most recent North Sea assessment (Quality Status Report) [20] where there remains a preoccupation with the levels, sources and fluxes of contaminants. This is something one might expect in the case of first assessments as exemplified by the recent GPA assessment of the Southeast Pacific [21] but not that for assessments made by a wholly developed state community such as that surrounding the North Sea.

There is one striking example of an intrinsically scientific, authoritative and valuable first assessment of a regional area – that for the Arctic completed in 1997 [12, 13]. The product from this exercise, albeit an expensive one, demonstrates that a first assessment can be completed in a thoroughly competent and comprehensive manner in just 3 years from its inception. Furthermore, this assessment does not just cover marine conditions but all environmental compartments of the Arctic: land, freshwater, atmosphere and sea. Its success is largely attributable to the commitment made by the governments of the eight Arctic States (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and the United States) to ensure the involvement of scientists covering a range of disciplines. Beyond this, little policy influence seems to have been exerted by the countries on those involved in the preparation of the basic assessment that covers a variety of subjects in great depth [13]. The Arctic Monitoring and Assessment Programme secretariat was able to go further and obtain the services of an expert writer and editor to prepare a popular and most readable summary [12] of the full report. It is this process that has come closest to date to the guidance regarding organization and commitment advocated by GESAMP for the preparation of marine environmental assessments (GESAMP, 1994).

Most recently, the adoption of the Global Programme of Action [22] has stimulated the conduct of a number of regional assessments and the formulation of associated Regional Programmes of Action to address the adverse effects of land-based activities on the marine environment. Regional LBA reviews for the Red Sea/Gulf of Aden, the Eastern African Region, the South-East Pacific, the Persian Gulf and Gulf of Oman, West and Central Africa, the Southwest Atlantic, the Caribbean, South Asian Seas, the South Pacific and the Northwest Pacific are in various stages of preparation .

3. GLOBAL ASSESSMENTS

3.1. GESAMP Assessments

Global reviews of the state of the marine environment have largely been the prerogative of GESAMP. Indeed its primary term of reference is the undertaking of periodic reviews of the state of the marine environment. The first GESAMP review was completed and published in 1982 [23] and the second in 1990 [24]. Both of these reviews were hampered to differing degrees by the limited availability of comprehensive regional reviews. Nevertheless, the most recent GESAMP review has been widely accepted as the most authoritative pronouncement on the state of the marine environment, especially from the perspectives of contamination and pollution. Indeed, the definition of "pollution" originated from GESAMP and, although now sadly outdated, it has, until recently, constrained the terms of reference of GESAMP reviews. Under this latter definition, both human activities and the adverse effects of these activities beyond those involving "the introduction of substances" to the marine environment took a back seat in the review process. GESAMP has been repeatedly unwilling to revise its outdated definition, largely because it has become so widely emulated in jurisdictions dealing with the impacts of man on the sea and various legal texts (*e.g.*, the UN Law of the Sea Convention). Nevertheless, the recent development of the Global Programme of Action for the Protection of the Marine Environment from Land-Based Activities adopted in Washington, D.C., in 1995 [22] and the induction of GESAMP into the associated assessment process, has necessarily resulted in a broadening of the implicit terms of reference of its new review activities. This was timely because GESAMP had fully recognized the relative severity of a wide range of human activities beyond those solely associated with the introduction of substances such as coastal development and marine resource exploitation. Thus, in a rather roundabout manner, sanity has eventually prevailed.

In 1996, GESAMP decided to commence planning for a new global state of the marine environment review to be completed in the year 2002 [25]. GESAMP had also reached the conclusion that there was a need for interim statements regarding the condition of the oceans in the periods between major state of the marine environment reviews. The GESAMP sponsoring agencies therefore decided to commission a working group and a process leading to the preparation of:

1. a first biennial statement on the condition of the marine environment to be issued in 1998;
2. a global assessment of the state of the marine environment from the perspective of land-based activities for the purposes of the GPA to be completed in 1999; and
3. a new major comprehensive review of the state of the marine environment to be completed in 2002.

Most global assessments are necessarily based on the analysis of regional assessments. In 1994, GESAMP, in recognition of the importance of increasing the number and specificity of regional assessments, published simple guidelines for their preparation [1]. Its motive in doing so was to encourage the preparation of new regional assessments, to improve their comprehensiveness and to promote the adoption of standardized contents and format. Unfortunately, either because these guidelines are so recent or they contain some unknown flaws, they do not appear to be being used. Most remarkable is the fact that the most recent regional assessments commissioned for GPA purposes are not adhering to these guidelines.

The GESAMP assessment process has started with the completion of a draft "Biennial Review" and a first draft of the Land-Based Activities Assessment for GPA purposes. The next "State of the Marine Environment Review will commence immediately following the completion of these documents in early 1999. The first Biennial Review will dwell on a number of emerging issues that will be dealt with in greater depth in the LBA and SOMA reviews depending on their sources (*i.e.*, land or marine). Among these are: coastal eutrophication and the role of atmospheric nitrogen; the changing input of nutrient nitrogen to the open ocean; endocrine disrupting chemicals; invasive species; overfishing on coral reefs; expanding coastal populations and tourism; climate and sea-level changes as marine pollution problems; the impact of climate change on marine fish populations; offshore drilling in deep waters; and decommissioning of offshore structures.

3.2 The Global International Waters Assessment

In 1997, the UNEP Coordination Office for the Global Environment facility (GEF) formulated a GEF project entitled "Global International Waters Assessment" (GIWA) [26]. This project, now funded by the GEF in the amount of US$ 6.7 Million and awaiting the identification of co-financing of US$ 7.3 Million, is to carry out a global assessment of International Waters from a range of perspectives. International Waters are those defined by GEF and include all marine waters and shared (i.e., riparian) freshwater bodies. The project will focus on the assessment of twenty-three issues grouped under five major concerns: freshwater shortage; pollution; habitat loss and modification; over-exploitation of fisheries and other living marine resources; and global change. It will incorporate a root-cause analysis in each of these areas to define the underlying reasons for existing problems and threats. These assessments will initially be carried out in 66 sub-regions within 9 major regions of the world. Table I shows the hierarchical breakdown for the western side of a single region, the North Atlantic, as an example. The project is expected to take about 3 years to complete and will comprise regional task teams with a global core team based in Kalmar, Sweden.

TABLE I WESTERN NORTH ATLANTIC AND MAJOR FRESHWATER CATCHMENT BASINS

Marine Area Level 1	**Marine Sub-Areas Level 2***	**Marine Sub-Areas Level 3**	**Freshwater Catchments Level 1**	**Freshwater Catchments Level 2**
Wider Caribbean	*Gulf of Mexico*		Mississippi Rio Grande Brazos Grijalva Colorado	
	Caribbean Sea		Magdalena	
Western North Atlantic	*Southeast Shelf*	Pamlico Sound	Pamlico Neuse	
	Northeast Shelf	Gulf of Maine	Androscoggin Penobscot	
		Bay of Fundy	St. John	
		Long Island Sound	Connecticut Hudson	
		Delaware Bay	Delaware	
		Chesapeake Bay	Susquehanna Potomac	
		Albermarle Sound	James	
	Scotian Shelf	Gulf of St. Lawrence	St. Lawrence	Great Lakes
	Newfoundland Shelf			
	Baffin Bay/ Labrador Sea/ Canadian Archipelago			
	East Greenland			
	West Greenland			
	Iceland Shelf			

Those involved in the design of the GIWA GEF Project acknowledged that GESAMP had already decided to undertake a new global assessment of the marine environment and requested GESAMP's cooperation in the GIWA assessment process. Similarly, the Scientific Committee on Problems of the Environment (SCOPE) has been invited to participate because it had, at about the same time, proposed to undertake a forward-looking review of threats to the marine environment and its resources. In addition, the Intergovernmental Oceanographic Commission (IOC), the Scientific Committee on Ocean Research (SCOR) and SCOPE (the latter two organizations being components of ICSU) are currently collaborating on an assessment of the state of marine science. This assessment will include an analysis of contemporary understanding of the oceans, identification of key scientific issues and the capability of science to satisfy policy and management demands into the first two decades of the 21^{st} Century. As of the end of June, 1998, a decision had been taken to establish a Joint Scientific Advisory Group which will meet in September, 1998. A workshop of 40-50 participants will be convened during the first half of 1999. Following the workshop, a small editorial group will assemble a final report by December 31^{st} 1999.

4. ADDITIONAL CONSIDERATIONS

The quality and effectiveness of assessments, particularly of regional marine areas, requires first and foremost a commitment from the countries in the region to the process. In a sense, this is a "chicken and egg" issue – the commitment can result in common agreement on the most important problems and substantial improvement in the targeting of corrective (intervention) measures. However, only an effective and comprehensive assessment, which depends on commitment, can demonstrate these benefits. The case of the Arctic Assessment [12, 13] is unique in this respect – it received an overwhelming commitment from the riparian states and it resulted in probably the most comprehensive and insightful assessments from which the countries could tailor future intervention and monitoring activities.

There continues to be, in some regions, a preoccupation with "pollution". It is really a preoccupation with contaminants and contamination. Assessments must focus on effects rather than the mere presence of chemicals. Furthermore, they should endeavour to be more comprehensive and give fair weight to the effects of human activities other than the introduction of substances into the marine environment.

Assessments provide the most valuable way of ensuring that monitoring programmes focus on the measurements needed to address priority issues. As GESAMP has recently pointed out [27] contemporary monitoring activities do not provide a basis for the detection and quantification of trends. This places society in the invidious position of being unable to determine if currently perceived threats actually transpire in the future. Worse, it also leaves society unable to determine if the intervention measures it adopts in favour of environmental protection are effective let alone cost-effective. If no improvement occurs, all the grand designs for protecting the oceans, its resources and amenities, will never be able to be judged on the basis of improvements in the condition of the oceans. This remains the most serious deficiency in current marine environmental protection activities. Only new surveillance approaches, such as that adopted in the design of the Global Ocean Observing System (GOOS) [28] offer the potential for rectifying this deficiency but will require substantial commitments of resources on a scale comparable with the global weather forecasting system.

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MODELLING THE DISTRIBUTION OF ^{90}Sr AND ^{137}Cs IN THE MEDITERRANEAN SEA (MTPII - MATER)

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Abstract

Within the frame of the MTPII-MATER project (MAST), the distribution of ^{90}Sr and ^{137}Cs in the Mediterranean Sea was modelled, as these radionuclides are useful tracers of water circulation. The Mediterranean Sea was divided into 81 boxes, corresponding to 21 regions, taking into account water mass circulation, bathymetry and data availability. Transfer rates were obtained from the MOM model run under MEDMEX conditions. The model was run with realistic inputs, which included weapons global fallout, Chernobyl ^{137}Cs, nuclear industry and river runoff. It was observed that existing data are scarce, especially in the eastern Mediterranean. In general, model predictions agreed well with observations, showing maximum concentrations in surface waters and maxima due to global fallout (^{137}Cs and ^{90}Sr) and to the Chernobyl accident (^{137}Cs only).

1. INTRODUCTION

1.1. The MTPII-MATER Project

Established by the European Commission in 1993, the MAST III Programme Mediterranean Targeted Project (MTP) represents a major effort in the understanding of the Mediterranean Sea today (both Western and Eastern basins). During the MTP I phase (1993-1996) 180 main scientists from 70 research centres in 14 European countries worked in 14 independent projects. During the MTP II phase, the MTP II - MATER Project integrates the efforts of 220 main scientists from 80 research centres in 11 European countries and 2 African countries.

The overall objective of the MTP II MATER is to study and to quantify the triggering and controlling mechanisms of mass and energy transfer between the different compartments (land-sea, sea-atmosphere, water-sediment, living-non living, pelagos-benthos), in contrasting trophic environments (from eutrophic to oligotrophic) of the Mediterranean Sea and to investigate the ecosystem response to such a transfer. The program is designed to assess the processes at various time and space scales, from the entire basin down to the local scale, and from daily processes up to inter annual variations.

The MATER project is an integrated and multiscale approach structured in seven research Tasks or scientific themes: Seasonal and interannual variability of the general circulation, Water mass formation processes and thermohaline circulation, Subbasin scale circulation and mesoscale dynamics, Processes controlling particle dynamics, Biotic and abiotic processes controlling biogeochemical cycles and fluxes, Benthic response to downward fluxes and Ecosystem studies. And five Work Packages or implementation areas: Basin scale process studies, Multidisciplinary studies in the western Mediterranean subbasin, Multidisciplinary studies in the Adriatic / Ionian subbasin, Multidisciplinary studies in the eastern Mediterranean and Ecological models and process studies.

1.2. Modelling

Within this large project, numerous pollutants are studied, mainly as tracers of oceanographic processes. Various marine processes, covering different time scales, can be studied using radiotracers, depending on the phenomena involved and the observational techniques used. Some natural radionuclides, such as ^{210}Pb and ^{7}Be, are continuously entering the marine environment in association with particles. On the other hand, some artificial radionuclides, such as ^{90}Sr, ^{137}Cs and ^{239,240}Pu entered the marine environment mainly during the sixties following nuclear tests in the Northern Hemisphere [1]. Both contributions, mostly of atmospheric origin, can today be traced in the marine environment using suitable techniques.

^{90}Sr and ^{137}Cs are, essentially, soluble elements in seawater [2] and have a radioactive half-life close to 30 years. Thus, they are useful radiotracers to study water mass transport in the oceans [3-5]. In this sense, the Mediterranean Sea has often been described as a small scale oceanographic laboratory [6] and offers a unique opportunity to test the suitability of using ^{137}Cs as a long-term radiotracer of water mass transport on a large scale.

The aim of this work was to develop a numerical model to contribute to the understanding of the main features of global circulation in the Mediterranean Sea, and to explain past and present levels of ^{137}Cs and ^{90}Sr. To do this, a 81 box model was developed and run with realistic input functions. Results were compared with ^{90}Sr and ^{137}Cs concentrations in Mediterranean Sea waters during the period 1954-1994 reported in the scientific literature.

2. METHOD

2.1. Model

The Mediterranean Sea was divided into 21 regions (Figure 1) and its water column was split into four layers, taking into consideration the different water types present in each region. The North Adriatic Sea was considered as one single box. Each box was carefully defined taking into account bathymetry, main water fluxes, input sources and data availability (used for model validation purposes).

The transfer rate between boxes was obtained from the MOM model run under MEDMEX conditions. The transfer of radiotracers between boxes was described by the advection-diffusion equation [7]. The numerical resolution of the differential equation was carried out with a FORTRAN program using the Runge-Kutta 4th order system. A full simulation needed a computation time of less than 1 minute with a personal computer provided with a 200 MHz Pentium processor.

2.2. Source term

The ^{90}Sr and ^{137}Cs sources considered in the model were global fallout from nuclear weapons, the Chernobyl accident, low-level liquid wastes from the nuclear industry and river runoff. As no long-term atmospheric ^{137}Cs sequences exist in Europe, its deposition was estimated from ^{90}Sr measurements, as its ratio has been shown to be almost constant in global fallout [1, 8].

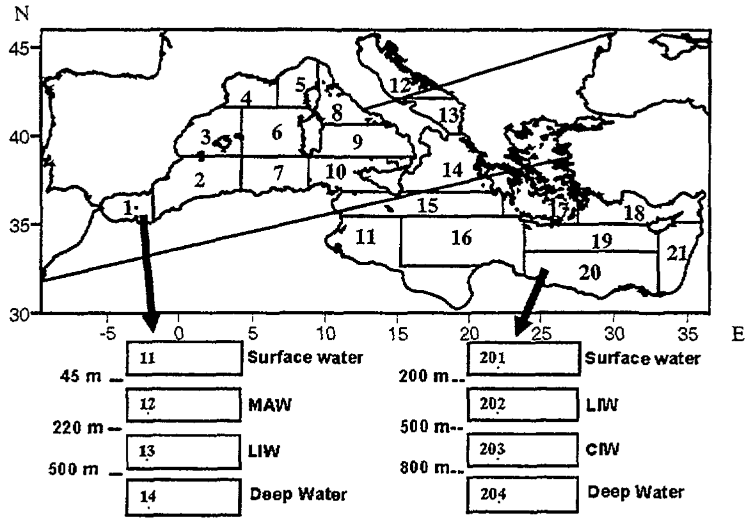

FIG 1. Map of the Mediterranean Sea showing the considered regions. Each region is vertically divided into several boxes, depending on the water depth and water characteristics

In 1986 the Chernobyl accident was responsible for a major input of, amongst other radionuclides, ^{137}Cs to Mediterranean surface waters. In this case, the deposition pattern was patchy, depending on the trajectories of the contaminated air plumes and rainfall during their passage [9]. Therefore, ^{137}Cs deposition was estimated from local studies found in the literature [10-14]. The input of Black Sea waters was described by Egorov and co-workers [15]. The ^{137}Cs input due to the nuclear industry has been reviewed during the Marina-Med project [16]. Finally, the ^{137}Cs input from river runoff was described by Fukai and co-workers [17].

2.3. Observations

The model was designed to predict ^{137}Cs annual mean concentrations in each box. In order to validate the model, these results were compared with observed mean values calculated from data available in each box, if any. The sources of information and data treatment are described in detail elsewhere [18]. Briefly, existing data in each box were explored for outliers, which were discarded in calculations. Then, the resulting distribution was tested for normality using the Kolmogorov-Smirnov non-parametric test, the results of which were always found to be positive. Finally, the mean and standard error of the mean was calculated for each box.

3. RESULTS AND DISCUSSION

3.1. Temporal evolution in surface waters

Surface water concentrations ranged from 0-87 Bq·m^{-3} and 0-19 Bq·m^{-3}, for ^{137}Cs and ^{90}Sr, respectively. In most boxes the most prominent feature was the existence of one ^{90}Sr and two ^{137}Cs concentration maxima, corresponding to the maximum air concentrations of both radionuclides due to nuclear weapons fallout (1963) and of ^{137}Cs due to the Chernobyl accident (1986). Maximum concentrations were observed in surface waters in all regions, generally decreasing as mean water depth increased. The predicted ^{137}Cs maximum concentration in the 60s ranged, across the Mediterranean Sea, from 7.54 Bq·m^{-3} in the Libyan Sea, to 16.7 Bq·m^{-3} in the Adriatic Sea. The predicted ^{90}Sr maximum concentrations ranged, from 4.16 Bq·m^{-3} in the Libyan Sea, to 8.62 Bq·m^{-3} in the Adriatic Sea.

Largest concentration gradients were observed during, and shortly after, the global fallout maxima. After the global fallout maximum was reached, levels decreased, first rapidly and later on more slowly, reaching pre-Chernobyl concentrations. ^{90}Sr concentrations decreased slowly until present. The maximum ^{137}Cs concentrations due to the Chernobyl accident, which ranged from 3.02-87.4 Bq·m^{-3}, showed largely different peak values because the deposition pattern was highly irregular. The maximum concentrations, 87.4 Bq·m^{-3} and 28.1 Bq·m^{-3}, were predicted to occur in the Adriatic Sea, where higher deposition was observed in the nearby terrestrial areas [14].Levels rapidly reached pre-Chernobyl values. The evolution of ^{137}Cs and ^{90}Sr inventories in the Mediterranean Sea are shown in Figure 2.

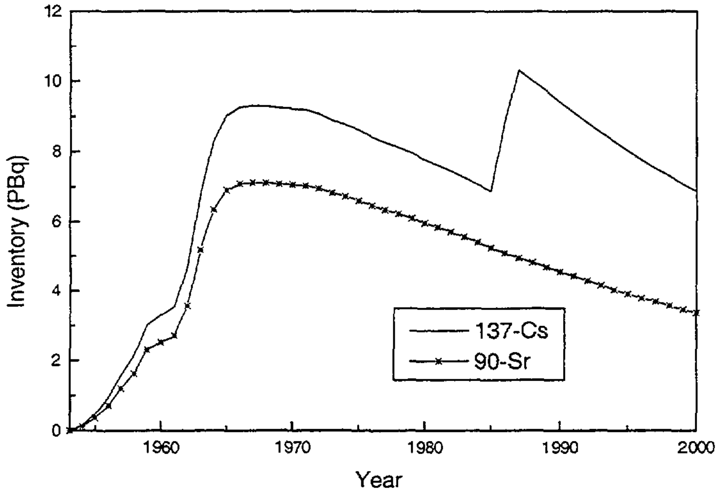

FIG 2. Modelled time evolution of ^{90}Sr and ^{137}Cs inventory in the Mediterranean Sea.

3.2. Temporal evolution in the water column

Because of the atmospheric origin of the contamination, maximum concentrations were observed in surface waters in all regions, generally decreasing as mean water depth increased. Largest concentration gradients were observed during, and shortly after, the global fallout maxima. Because ^{90}Sr and ^{137}Cs entered underlying waters essentially by mixing with surface waters, fallout maxima were usually delayed in deeper waters. This delay was longer as mean water depth increased. For example, in the Central-Occidental basin, global fallout maxima occurred during 1963 in surface waters, during 1965 in the second layer (Mixed Atlantic Waters), and during 1966-67 in the third layer (Levantine Intermediate Waters).

Before the Chernobyl accident, concentrations in the second layer progressively approached those in surface waters and were, in all cases, almost identical just before the accident. Predicted concentrations in the third layer showed a maximum much later than surface waters. The relative importance of this maximum was variable, and it was almost undetectable in some regions such as the Thyrrenian Sea, the Levantine Basin and the Libyan Sea, where an almost stable concentration was reached. In the fourth layer (Very Deep Mediterranean Waters), levels were in general very low and were steadily increasing until the present.

After the Chernobyl accident, new vertical concentration gradients appeared only for ^{137}Cs. Although the accident also affected the second layer waters, pre-Chernobyl conditions were rapidly attained and concentrations in the first two water layers were again equal by the end of the modelled period in most regions. An increase in third layer waters concentrations was also predicted for most regions, while a very low impact was predicted for very deep waters.

3.3. Model validation

The model was validated by comparison with annual mean concentrations of ^{137}Cs in Mediterranean Sea waters [17]. An important conclusion of this work was that, not unexpectedly, the number of available data points for model validation was limited. In general, existing data are dispersed over the whole basin and, except in the Adriatic Sea, no long-term series exist. This is an important limitation for the validation of any model using radiotracer data.

An example of mean annual ^{137}Cs concentrations measured in surface waters is presented, together with model predictions, in Figure 3. An 80 % of the measured data are in the range of values predicted by the model. The type of model presented here is especially well suited to describe systems in which temporal and spatial gradients are not large. In the contrary case, a higher resolution model is needed.

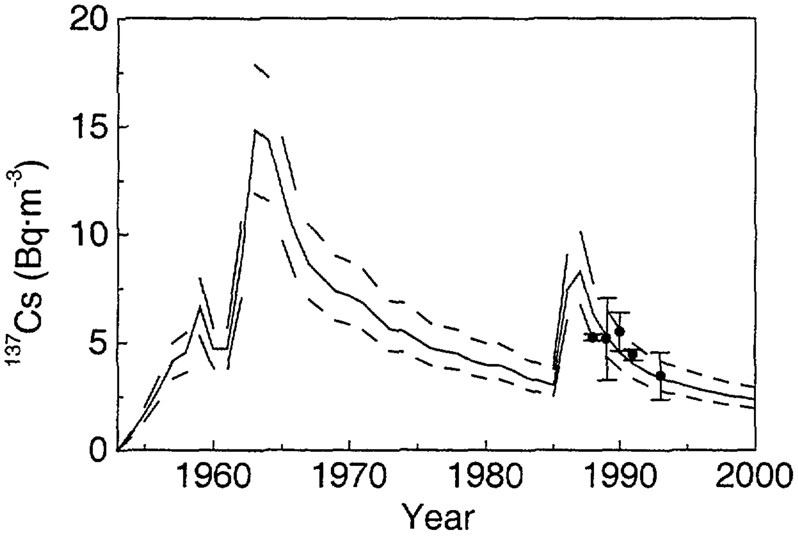

FIG 3. Mean annual ^{137}Cs concentrations observed in Mediterranean Sea surface waters (Catalan Sea) and model predictions. Dotted lines show a 20 % uncertainty estimation of the model.

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^{90}Sr, ^{137}Cs, ^{238}Pu, $^{239+240}$Pu AND ^{241}Am IN MATRICES OF THE TERRA NOVA BAY ECOSYSTEM (ANTARCTICA)

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The Radioecology Laboratory of Parma University has been engaged in marine Mediterranean researches since 1960. Several samples of seawater, sediments, plankton, vegetable and animal organisms collected in the Ligurian, Northern and Southern Thyrrenian, Ionium and Adriatic Seas have been analyzed during the past years. Concentrations of anthropogenic radionuclides in the marine environment were particularly relevant in the period 1962 - 65 derived from the fallout of nuclear atmospheric tests. More recently, high concentrations were determined in 1986 after the Chernobyl nuclear power plant accident.

The involvement of University of Parma by the Radioecology Laboratory in Antarctic research has started in 1987 in the framework of the Italian National Program for Antarctic Research (PNRA) - Environmental Contamination Sector. Since that period and particularly with the opening of the Italian antarctic Base, our interest has moved to the Terra Nova Bay environment (Ross Sea) with the aim of a chemical and radioactive characterization of the area. In fact, the interest for radioecological investigations in the Antarctic Ross Sea has been driven mainly by two basic reasons: the particular characteristics of this polar ecosystem and secondly, for having longly been considered as an unpolluted continent. Special emphasis has been put on Cs-137 data since it has always been the most abundant radionuclide detected [1,2,3]. More recently, the radioanalyses have been extended to the other fission product Sr-90 and transuranic products (Pu-238, Pu-239+240, Am-241). In addition, natural radionuclides such as K-40, Pb-210, Th-232 and U-238 have also been detected in sediment samples

Samples were collected during seasonal scientific expeditions at Terra Nova Bay - Ross Sea (Fig. 1) in a ten year period (1987 - 1996) Natural radionuclides such as Po-210 in ice cores [4] and K-40, Th-232 and U-238 have also been detected in sediment samples and presented elsewhere [1,2].

Besides the classical techniques for gamma emitters methods for radiochemical analyses of plutonium and strontium are reported in [3]. A sensitive and reliable new method [5] for the sequential determination of plutonium, Sr-90 and Am-241 (besides Cs-137) has been used for the first time. A device for sampling and concentrating large volumes (3000 liters) of seawater has also been tested for the first time in Antarctica during the 1995-96 campaign. Such instrument simultaneously collected surface seawater and passed it through NCFC and MnO_2 beds; this parallel isolation was able to determine Cs-137 and Pu respectively.

The results have demonstrated that the contamination levels of the Antactic continent is generally lower than that detected in the Mediterranean area during the same period (Table 1).

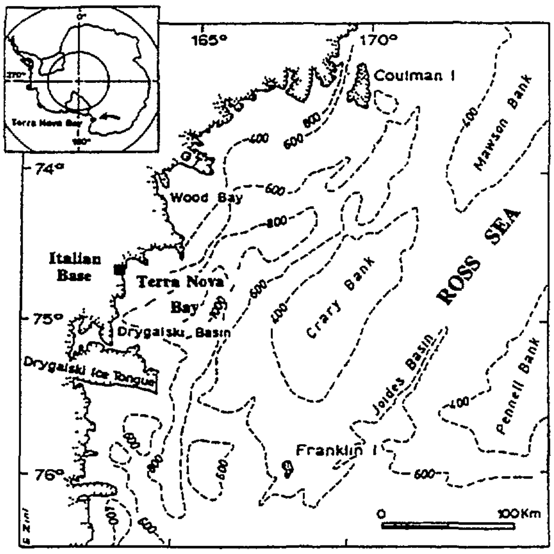

FIG. 1. Study area at Terra Nova Bay.

TABLE I. ANTHROPOGENIC RADIONUCLIDES CONCENTRATIONS (Bq/m^3 OR Bq/kg DRY WEIGHT) DETECTED IN ANTARTIC AND MEDITERRANIAN SAMPLES

Matrix	Cs-137	Sr-90	Pu-239+240	Pu-238	Am-241
Antarctica (Ross Sea 1990-96)					
Water	0.44 - 0.83	-	0.0058 - 0.00071	0.00013	0.00053 - 0.0025
Sediment	0.14 - 0.26	<0.10 - 0.36	0.0056 - 0.0908	0.0014 - 0.0044	0.0024 - 0.044
Organisms	0.18 - 1.28	0.080 - 0.11	<0.0022 - 0.045	<0.0022 - 0.013	0.0006 - 0.0089
Mediterranean (Adriatic Sea 1990-96)					
Water	3.36 - 5.18	-	0.013 - 0.025	0.0009 - 0.0074	-
Sediment	1.50 - 18.5	<0.16 - 0.51	0.080 - 0.683	0.004 - 0.022	0.036 - 0.188
Organisms	1.00 - 2.57	-	<0.01 - 0.034	0.0020	-
Mediterranean (Po river Delta 1990-96)					
Water	2.8 - 4.3	-	-	-	-
Sediment	9.90 - 31.3	<0.16 - 5.80	0.68 - 1.23	0.02 - 0.03	0.037 - 0.042
Organisms	1.00 - 9.00		0.034	0.0020	-
Mediterranean (Aeolian Islands 1994-95)					
Water	2.92 - 3.2	-	-	-	-
Sediment	0.32 - 7.8	0.5 - 1.5	0.11 - 0.23	0.0066 - 0.0089	0.029 - 0.161
Organisms	-	-	-	-	-

The activity levels of Pu-239, Am-241, Sr-90 and Cs-137 in Antarctic sediments were about 5-10 times lower than in Northern Adriatic Sea and Southern Thyrrenian in the period 1992-94 [6]. The data were even much lower than the Po delta concentrations because of the particular accumulation mechanism of this adriatic estuary. In particular, the radionuclide ratios revealed that Am, Cs, Pu and Sr reached the Antarctic continent as a result of nuclear weapons tests. However, the Pu-238 concentrations were higher than expected in the Antarctic. The Pu-238/Pu-239 ratio was about 8 times higher than in the northern hemisphere and it could be inferred that the major part of Pu-238 was originated from the SNAP-9A satellite accident.

In spite of the general low contamination of the Antarctic environment, some interesting results in relation to particular ecological processes and biogeochemical cycles, are presented

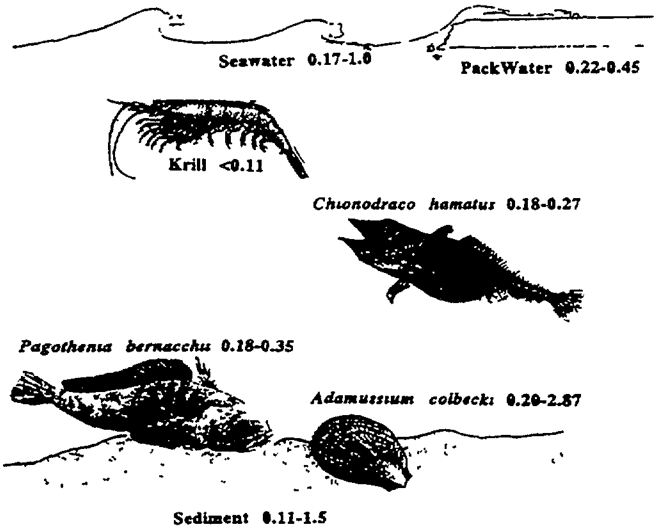

FIG. 2. Ranges of Cs-137 concentrations (Bq/m^3 or Bq/kg dw) in abiotic and biotic samples of Antarctica.

Concentrations were generally higher in the coastal area where terrigenous transport and water run off from ice melting influences the activity levels especially in sediment samples. Increasing concentrations of Cs-137 were detected in *Adamussium colbecki* (antarctic scallop) during summer months as a result of major trophic activity. The transfer path from this bivalve to the benthic fish *Pagothenia bernacchii* has also been followed. A seasonality in the organisms accumulation patterns has been demonstrated. Cs-137 Concentration Factors (C.F.) have been calculated for each single species. C.F. for the bivalve were much higher (145-920) than the data reccomanded by Iaea (30) [7] and this is probably due to major ecological and physiological differences. For the fish the results were in normal ranges. In fig 2 a complete representation of Cs-137 distribution in the abiotic samples and within the trophic webis reported. A direct link between *Adamussium* and *Pagothenia* can be observed.

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HIGH SCAVENGING RATES IN THE WESTERN ARCTIC OCEAN REVEALED BY TIMS MEASUREMENTS OF NATURAL RADIONUCLIDES

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Naturally occurring particle-reactive isotopes of the uranium and thorium decay series are useful tracers of scavenging processes and the fate of reactive contaminants in the marine environment. The first measurements of long-lived protactinium and thorium isotopes in the Canada Basin of the Arctic Ocean, at the CESAR Ice Station on the Alpha Ridge, revealed higher concentrations of ^{230}Th and ^{231}Pa than previously observed in other ocean basins [1]. These observations were consistent with prevailing hypotheses about scavenging in the Arctic, specifically that scavenging was very slow in areas of permanent ice cover, and thus particle-reactive species, both natural and anthropogenic, would build up to high concentrations. Arctic deep waters might then constitute a source of contaminants to the Nordic Seas and North Atlantic Ocean via the Fram Strait.

A more recent study in the Eurasian Basins of the Arctic by [3] showed lower concentrations of both ^{230}Th and ^{231}Pa than at the Alpha Ridge, indicating the spatial heterogeneity of productivity and particle flux in the Arctic. One station in the Makarov Basin exhibited high concentrations, however, and the picture of slow scavenging in the western Arctic remained. Recent developments in the use of thermal ionization mass spectrometry (TIMS) to measure low abundance, long-lived uranium series nuclides in seawater [3,4.2], combined with icebreaker expeditions to the western Arctic, now allow for a tremendous expansion of the data set for this region, and a more extensive testing of these hypotheses.

[2] reported TIMS measurements of ^{230}Th, ^{232}Th, and ^{231}Pa in one-liter seawater samples from two stations in the Beaufort Sea, one on the slope and one in the permanently ice-covered deep basin. These authors found lower concentrations of ^{230}Th and ^{231}Pa in the Beaufort Sea than at comparable depths at the CESAR Station, and average ^{230}Th and ^{231}Pa residence times for the deep waters (>900 m) of 17 and 110 years, respectively, similar to other ocean basins (including the Eurasian Arctic). Model results were consistent with typical suspended particulate matter concentrations and particle settling rates. ^{232}Th concentrations, which are used as indicators of detrital material, suggested that offshore advection of particulate material from the shelves may contribute to scavenging hundreds of kilometers from the ice edge.

Samples were also collected for TIMS thorium and protactinium measurements at three additional stations — one in the Canada Basin, one in the Makarov Basin, and one at the North Pole — on the Arctic Ocean Section (AOS) cruise in 1994. TIMS analyses were carried out in March and April, 1998. The concentrations are intermediate between those of the Beaufort Sea and the Alpha Ridge, suggesting that the Alpha Ridge is anomalous in its very low scavenging rates, and that the potential for export of particle-reactive contaminants from the Arctic to the North Atlantic is less than previously hypothesised.

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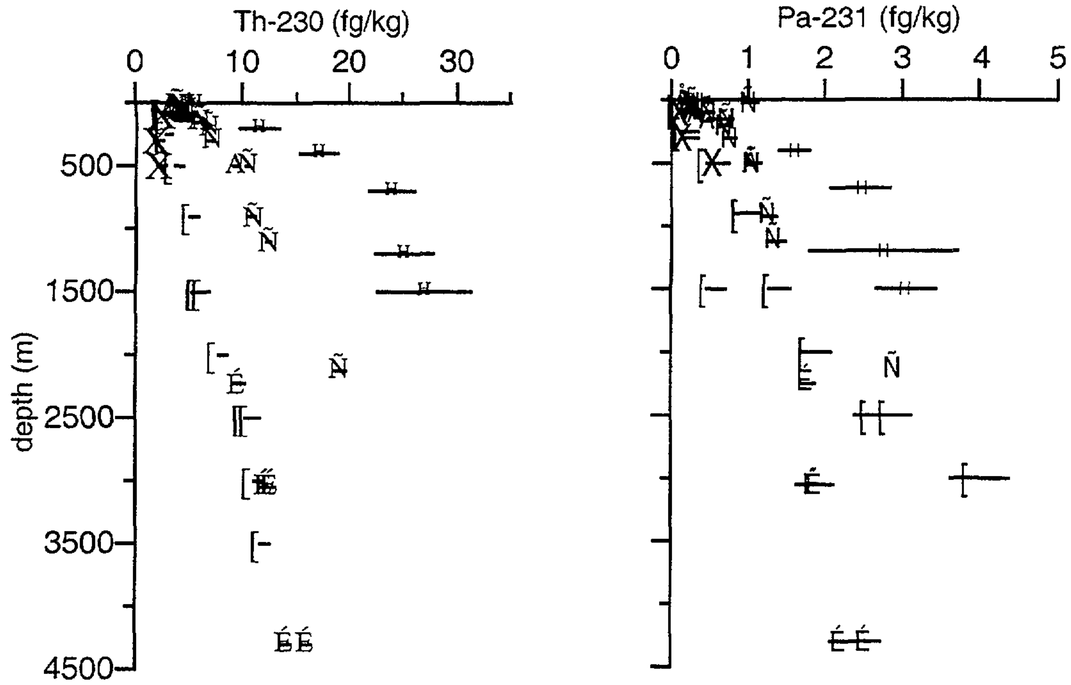

FIG 1. Vertical profiles of total ^{230}Th and ^{231}Pa, measured by TIMS at Stations AO1 ([) and AM10 (X) in the Beaufort Sea [2] and Stations 18 (A), 25 (G), and 35 (E) of the 1994 Arctic Ocean Section (new data), shown with total ^{230}Th and dissolved ^{231}Pa data from the CESAR Ice Station at the Alpha Ridge (H) determined by alpha counting [1].

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XA9951938

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RADIOECOLOGICAL STUDIES IN THE BARENTS SEA

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Since 1992 the Institute of Fisheries Ecology has been monitoring radioactivity in fish from Barents Sea, mostly taken as random samples from hauls on board of commercial trawlers in the western part near Bear Island and from Northcap Bank. Soon cod was selected as reference fish because of its widespread existence and because of its always slightly elevated concentrations of ^{137}Cs compared with other species. Inspecting data refering to the same year but different areas or to the same area but different years, these concentrations in the biological samples show a broad distribution. Statistical data always spread around their mean. That may result from different sources. It can be entirely a random distribution of single values, it can be a not predictable annually or regionally varying influence on the whole ecosystem, or it can be a systematic variations of the investigated objects. All these effects together make it difficult to compare systems based on random samples. Wrong interpretations may follow, which in hypothesis tests are called errors of 1. or 2. type. These errors affect the power of a test.

Results of further cruises with ‚FFS Walther Herwig III‘ in 1994 and in 1997 indicated a systematic relation between the ^{137}Cs concentration in cod fillets and the length of these fishes. An increase of these concentrations with fish length was observed. Such a correlation was verified by russian investigations, in the meantime for cod, too. In the length range from 25 cm to 115 cm, e.g. the ^{137}Cs concentrations increased four times in fishes from the same haul. The power of a test can be improved taking into account fish length as a covariable. As a consequence, with equal tolerated error probability, smaller differences of means can be declared.

An analysis of covariance was performed with the SAS procedure GLM. A cubic regression of length was included to analyse the logarithms of the ^{137}Cs concentrations for regional differences. For these log-transformed data the residuals show the necessary normal distribution. A cross term for linear regression and region was allowed. The only significant change for this cross term resulted for Northcap Bank cod. For the other regions one equal regression parameter was sufficient. Therefore the fitted curves for Spitzbergen, Bear Island, and Central Bank are quite similar with always increasing trend. In contrast, for Northcap Bank, there is an almost horizontal line between 50 and 70 cm length. At Northcap Bank, the smaller fishes seem to have higher ^{137}Cs concentrations relative to larger ones than in the other regions. In all areas fish length is an important biological parameter for the ^{137}Cs concentration in cod fillet.

We found different length distributions of cod stocks in the distinct investigation areas and different means for ^{137}Cs concentrations in fillets. But the influence of length on concentration could be considered and more general results could be derived. It became evident that everywhere in the monitored part of the Barents Sea, between Bear Island and Central Bank, obviously similar low levels of ^{137}Cs in cod fillet were present. In 1997 e.g. cod of length 70 cm has got only 0.3 Bq/kg ww. Differences in the means between Bear Island and Spitzbergen or between Bear Island and Central Bank were found in the range of 10% to 15%, with increasing concentrations from Spitzbergen to Central Bank. It seams to be more probable that the small differences between ^{137}Cs concentrations in cod fillet from different catching areas detected in 1997 find an explanation in local differences in the food web rather than they hint at further sources of radioactivity [1]. Results of model calculations make it very unlikely that radioactivity, e.g. from dumping sites in the Kara Sea, effects the levels in the Barents Sea noticeably [2]. Besides with nuclear fallout the Barents Sea is mainly loaded with radionuclides from the European nuclear reprocessing plants [3, 4].

Between 1994 and 1997 ^{137}Cs concentrations in cod fillets from Barents Sea decreased more than those in water [5]. In 1994 we calculated a concentration factor from water to cod fillet of just below 200 l/kg for cod of medium length. In 1997 the factor was reduced to almost 100 l/kg, which corresponds well with the recommended value for North Sea cod. This variation of the concentration factor agrees quite well with a reported [6] time dependence between 28 l/kg and 182 l/kg, observed for cod fillet from the Barents Sea from 1979 to1994.

Acknowledgements

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^{239,240}Pu, ^{137}Cs AND ^{90}Sr IN BOTTOM SEDIMENTS OF THE KARA SEA. THE ATTEMPT TO RECONSTRUCT RATE OF THE RADIONUCLIDES SUPPLY TO BOTTOM SEDIMENT IN THE PAST

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Despite the availability of extensive information about the levels of technogenous radioactive contamination of the Kara Sea, the problem on assessment of contribution of different sources into forming the total radioactive contamination of this basin remains to be of current interest. Discharge of the largest Siberian rivers – Ob' and Yenisey being exposed to the impact of three Russian plants for weapon plutonium production - is the potential contributor of contamination in the Kara Sea. In the present work, emphases is given to the role of one of these rivers, i.e. Yenisey River, in transfer of the long-lived radionuclides ^{239}Pu, ^{137}Cs and ^{90}Sr into the Kara Sea.

^{239,240}Pu, ^{137}Cs and ^{90}Sr contents were determined in bottom sediments of the Kara Sea and Yenisey

Pu-239,240 and Cs-137 in surface sediments of the Kara Sea [Bq/kg] and their ratio.

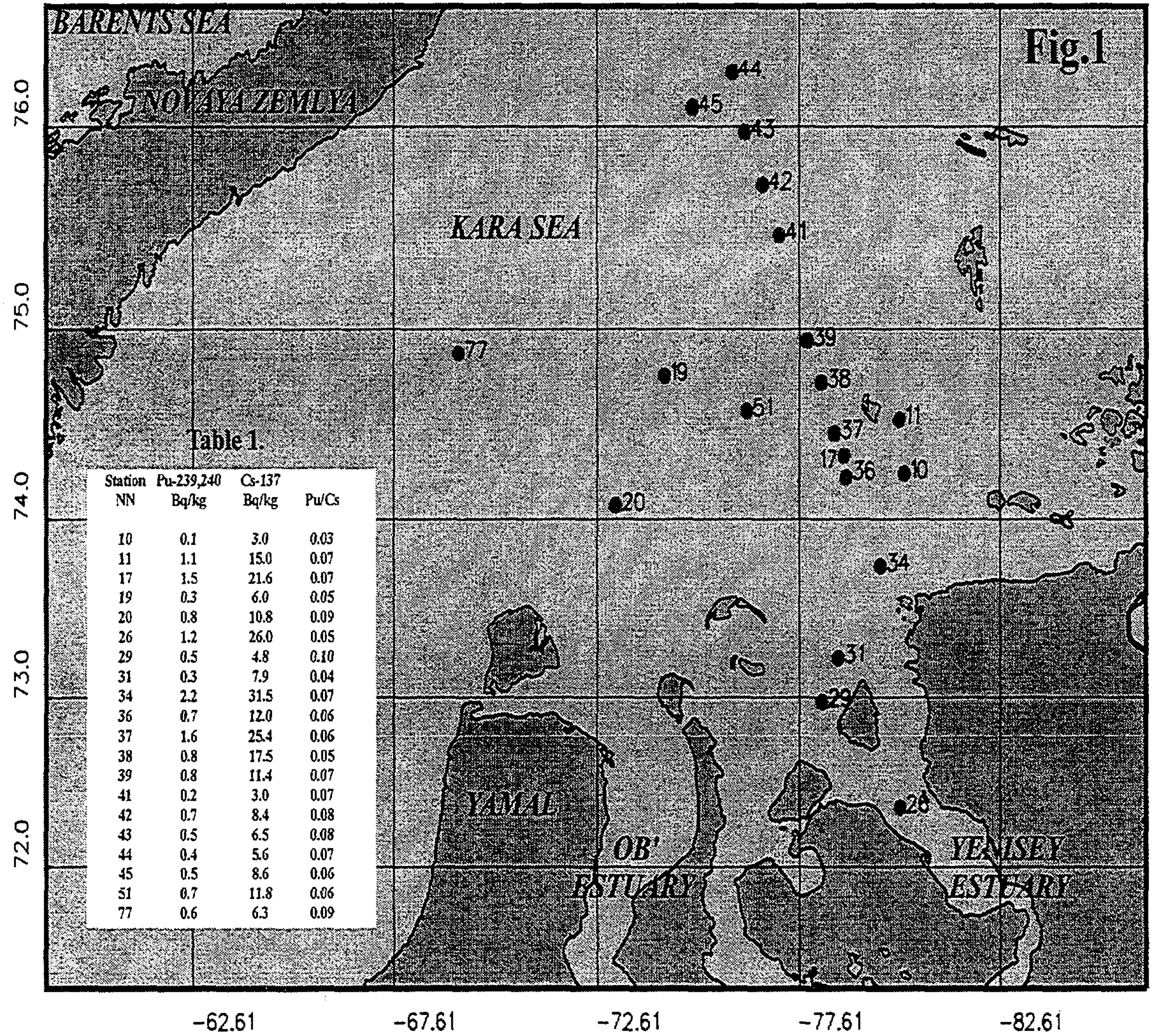


Table 1.

Station NN	Pu-239,240 Bq/kg	Cs-137 Bq/kg	Pu/Cs
10	0.1	3.0	0.03
11	1.1	15.0	0.07
17	1.5	21.6	0.07
19	0.3	6.0	0.05
20	0.8	10.8	0.09
26	1.2	26.0	0.05
29	0.5	4.8	0.10
31	0.3	7.9	0.04
34	2.2	31.5	0.07
36	0.7	12.0	0.06
37	1.6	25.4	0.06
38	0.8	17.5	0.05
39	0.8	11.4	0.07
41	0.2	3.0	0.07
42	0.7	8.4	0.08
43	0.5	6.5	0.08
44	0.4	5.6	0.07
45	0.5	8.6	0.06
51	0.7	11.8	0.06
77	0.6	6.3	0.09

River estuary (Fig 1) which were taken during expeditions on research ships "D.Mendeleev" and "D.Ovtsyn" in 1993, as well as in flood-plain and bottom sediments of the Yenisey River the samples of which were taken during annual expeditions along the river. Table I presents the data on ^{239,240}Pu and ^{137}Cs content in surface layer of bottom sediments of the Kara Sea; Fig.2 shows the connection between distribution of these radionuclides in bottom sediments. Fig.3 illustrates the vertical distribution of ^{239,240}Pu and ^{137}Cs in bottom sediments (stations 31 and 34). It could be concluded from Figs 2,3 and Table 1 that there is a direct correlation dependence between distribution of these radionuclides in surface layers and vertical section of bottom sediments taken in the Kara Sea. Similar data were obtained in [1] River delta. The observed similarity in behavior of ^{239,240}Pu and ^{137}Cs is substantiated by our data on the high values of distribution coefficients (10^5 - 10^3) of these radionuclides between aqueous phase and bottom sediments of the Kara Sea, as well as the data confirming the high stability of ^{239,240}Pu and ^{137}Cs in sea sediments.

Similarity in migration behavior of plutonium and cesium on their transfer with solid phase of the Yenisey river run-off into the Kara Sea is confirmed also by the data presented in Tables I and II. Thus, consideration of these data shows that ^{239,240}Pu and ^{137}Cs enter efficiently into the structure of the suspensions and bottom sediments of the Yenisey River with high efficiency (Table I). The data of Table II show that ^{239,240}Pu is most firmly bound with the structure of the bottom sediments and its return into aqueous phase is practically ruled out. As to ^{137}Cs, such secondary transfer from bottom sediments into river water is possible, although on a limited scale.

The relationship among the vertical distribution of ^{239,240}Pu, ^{137}Cs and the age scale as applied to two samples of bottom sediments of the Kara Sea (Figs 1,3) has revealed that the surpassing of present level of supplying these radionuclides into the studied sediments was caused by the most intense tests of nuclear weapons at the beginning of the sixties.

TABLE I. DISTRIBUTION COEFFICIENTS (Kds, ml/g) FOR Cs-137 AND Pu-239,240 BETWEEN BOTTOM SEDIMENTS AND WATER PHASES OF YENISEY RIVER AND KARA SEA.

	Radionuclide	Distribution coefficients (Kds)	
		Our data	* Reference data
Yenisey River	Cs-137	$2,5*10^4 - 8,0*10^4$	
	Pu-239,240	$(1,0 - 4,2)*10^5$	
Kara Sea	Cs-137	$1*10^3$	$3*10^3$
	Pu-239,240	$6*10^4$	$1*10^5$

* Data of the Russian - Norwegian expedition

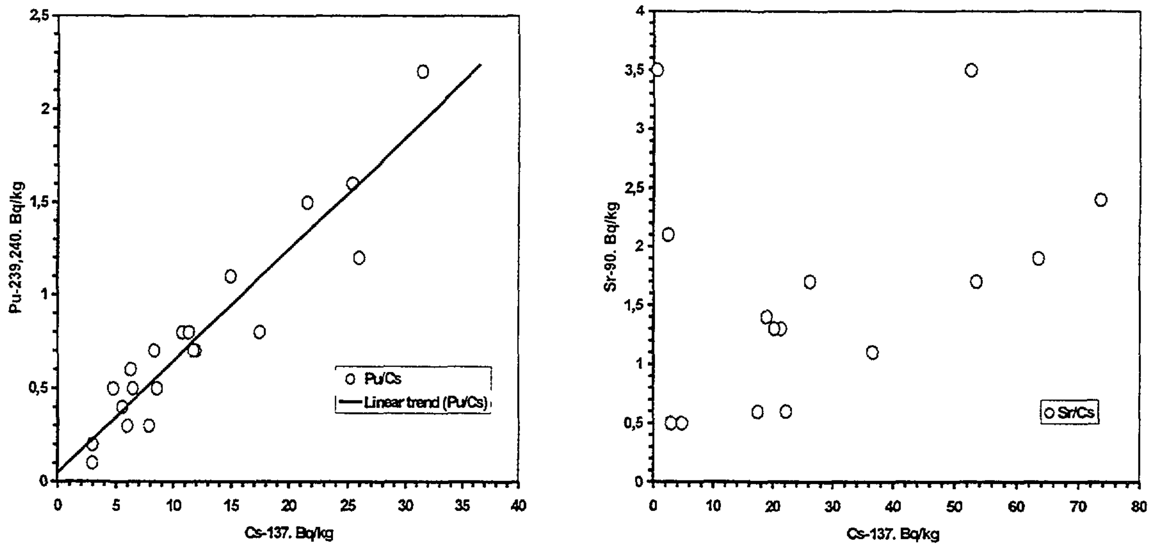
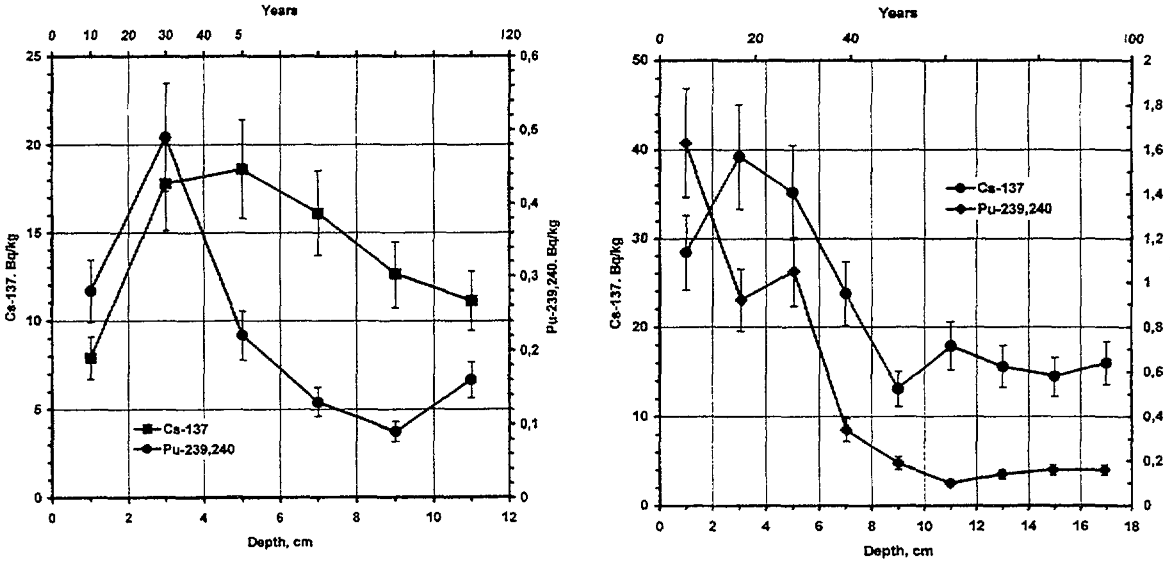


FIG. 2. Correlations between Cs-137 and Pu-239,240 and Cs-137 and Sr-90 contents in surface bottom sediments

^{90}Sr content in surface sediments of the Yenisey Gulf and the Kara Sea varies within much more narrow range as to ^{137}Cs and ^{239,240}Pu content. No direct correlation in distribution of ^{90}Sr and ^{137}Cs in surface sediments was detected. Distribution coefficients of ^{90}Sr between bottom sediments and aqueous phase calculated by us for the Kara Sea and Yenisey River are much less (10^1 - 10^2) than these values as to for ^{239,240}Pu and ^{137}Cs.(Table II).

TABLE II. DISTRIBUTION (%) OF Pu-239,240 AND Cs-137 BETWEEN POTENTIAL-MOVABLE AND FIRMLY BOUND FORMS IN BOTTOM SEDIMENTS OF THE YENISEY RIVER (HORIZON 0-5 cm, SOLID PHASE/LIQUID PHASE = 1:5).

Distance from MChC	Potential-mobile forms 1M NH_4COOH_3		Acid-soluble form 6M HCl		Unsoluble forms	
km	Pu-239,240	Cs-137	Pu-239,240	Cs-137	Pu-239,240	Cs-137
6,5	<0,1	29±3	61±9	46±6	39±5	46±6
9,0	1,2±0,2	11±1	65±6	21±2	33±4	68±5
15,0	1,3±0,2	43±3	61±10	51±5	38±3	5±1
19,0	2,0±0,3	13±1	49±5	20±2	49±5	66±7



Station 31 Sedimentation rate–1,1mm/y (Pb-210) Station 34 Sedimentation rate–1,8mm/y (Pb-210)

FIG.3. Vertical distribution of Cs-137 and Pu-239,240 in bottom sediments (Station NN 31 and 34) with decay correction for Cs-137

In conclusion we can say:

- The migration of ^{239,240}Pu and ^{137}Cs with solid phase of river run-off extends over large areas: this is predominant mechanism of supplying these radionuclides by the Yenisey River into the Kara Sea bottom sediments which are forming under impact of solid phase of the Yenisey river run-off.
- The main part of ^{90}Sr migrates in soluble form with run-off of the Yenisey River. This is also dominant species of ^{90}Sr occurrence in the Kara Sea.
- The surpassing of present level of ^{239,240}Pu and ^{137}Cs supply into these sediments (30-40 years ago) was caused by the most intense tests of nuclear weapons at the beginning of the sixties.

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REAL AND ALLEGED HAZARD OF RADIOACTIVE CONTAMINATION OF SEAS CAUSED BY ACTIVITIES OF RUSSIAN NUCLEAR FLEETS

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The current paper addresses the assessment results of the degree of danger caused by radioactive contamination of seas by wastes from the activities of nuclear fleets compared to the results obtained in other works , specifically , in the IASAP program. The leading institution in Project 101, ISTC is the Lazurit Central Design Bureau Open Joint-Stock Co. (Nizhny Novgorod) . The co-executors are RRC Kurchatov Institute, OKBM, NIKIET , OKB Hydropress , SPA Typhoon. Besides that experts from the Naval institutions , State Research Center Krylov Shipbuilding Research Institute , Prometei Research Institute, Central Design Bureau Iceberg and others were involved into the work. Project 101B, while covering only the marine part of the problem associated with the activities of the Navy and Civil Fleet, was co-ordinated with Project 245 in part of forming the databases as the scope of activities of the latter project included global aspects of radiation legacy of the former USSR.

Computer databank regarding the sources of actual and potential radiation contamination of seas was established in the course of the Project execution.
Information about 600 objects was included into the databank. It covered:

-21 nuclear reactors with spent nuclear fuel and without spent nuclear fuel dumped at sea;
-155 decommissioned nuclear submarines ;
-2 decommissioned ice-breakers ;
-15 floating technical bases to support nuclear submarines and ice-breakers ;
-29 tankers for liquid radioactive wastes, floating cells, controlling dosimetric vessels etc.;
-355 packings containing 33,000 units of various equipment and structures.

The database on the environment includes information about the radioactive contamination of dumping sites (based on the monitoring data) as well as information of the oceanographic nature and the biocenosis in the dumping site areas as well as of the global nature in the conditions of open sea along the routes of the forecast migration of radionuclides in case of their release from sources.

Analysis of structural peculiarities of objects with non-offloaded nuclear fuel dumped at the sea bottom as well as measures of their conservation adopted in the 1960-s before dumping while using the reactor cavity filling with furfurol and cementing of reactor spaces enables to draw the unambiguous conclusion about the principal impossibility of salvo releases of radionuclides into the environment which might have caused deterioration of its radioecologic situation. Risk assessment for the population of the Nenets National District caused by dumping of reactors in the Kara Sea was performed within the Project.

The executed assessment enables to claim that sources of radioactive wastes dumped in the Kara Sea do not and will not represent a radioecologic danger for the population and nature of the Nenets National District within 1,000 years to come and the maximum annual doses of 0.2..0.3 Sv per annum reached by Year 3000 will make 0.03..0.04% of the currently formed levels of contamination on the territory of the Nenets National District which is considerably lower than the standards established by the Norms of Radiation Safety -96. The potential risk in Year 3000 will make from 0.005 up to 5% of the actual current risk level formed by global fallouts of radionuclides which is much lower than stipulated by the Norms of Radiation Safety (NRB-96).

The analysis of the after-effects of accidents during storage of nuclear submarines with offloaded cores enables to make a conclusion about their extremely inconsiderable impact on the environment which , as in the previous case with the objects dumped at the sea bottom, also enables to consider this danger an alleged one.

The danger caused by floating technical bases containing such radioactive material as spent nuclear fuel is quite evident. Taking into account the fact that a floating technical base can contain up to three cores simultaneously , the total activity of spent nuclear fuel stored at the floating technical base will be about 4,8 10^{15} Bq. Taking into account the fact that contrary to the nuclear submarines , a number of shielding barriers preventing propagation of radionuclides from the spent nuclear fuel is absent on the floating technical base in case of their dumping (there is no pressure hull of the reactor compartment , no reactor hull) as well as the availability of conditions for enhanced corrosion of the spent heat-emitting assembly casings (damp air and temperature elevation caused by the deterioration of heat-takeoff in case of "dry" storage) compared to their storage in the reactor in the primary circuit water without contact with air , release of radionuclides from the floating technical bases in case of their dumping will be considerably higher than during dumping of the nuclear submarine.

Taking into account the convservation measures adopted before dumping of reactor compartments and nuclear submarines with emergency reactor cores , no salvo releases of radionuclides into the environment can be expected , operations for their recovery and re-dumping are not justified from ecological , technical or economic points of view. It is expedient to perform recovery from the sea bottom of the packing with the container of the shielding assembly from the nuclear icebreaker «Lenin».This packing alone, its mass being about 350 tons, contains about 60% of the total activity of all spent nuclear fuel dumped in the Kara Sea. According to the Lazurit assessment the cost of the recovery operation is USD 8-10 million. Nuclear submarines with offloaded cores do not represent a real danger and can be recommended for storage during 50-70 years in the slightly submerged state before the follow-on disposal (scrapping). Floating technical bases with spent nuclear fuel represent the maximum real danger. The first -priority task is to offload spent nuclear fuel into the shore storages. The computer dababases on sources of radionuclide contamination and the environment developed within project 101, ISTC, can be submitted to the experts at their inquiry via Internet.

IAEA-SM-354/8P

PHYSICO-CHEMICAL SPECIATION OF PLUTONIUM IN ARCTIC SHELF WATERS AT THULE, NW GREENLAND

XA9951941

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Data on the physico-chemical speciation of plutonium in Arctic shelf waters, gathered in the course of a collaborative research expedition to NW Greenland in August 1997, are discussed here. Specifically, we report the results of analyses carried out in the marine zone close to the Thule air base, where a US B-52 bomber carrying four plutonium-bearing weapons crashed on the ice in 1968, causing the release of kilogramme quantities of insoluble plutonium oxide to the snow-pack and underlying seabed sediments. For comparison, we also include data gathered at Upernavik, a location remote from the accident zone (Fig. 1).

Surface and sub-surface sea water samples (~150 litres) were collected from aboard the F.S. *Adolf Jensen* at the stations shown. The samples were immediately filtered (0.45 μm) and the oxidation state distribution of plutonium in the dissolved phase determined *in situ* using a technique based on the sequential co-precipitation of reduced plutonium species with small amounts of ferric hydroxide [1, 2]. To quantify the yields and monitor the cross-over between oxidised and reduced species during separation, two isotopic tracers in different oxidation states, ^{242}Pu(IV) and ^{236}Pu(VI), were added to each sample, which was then made 0.3M in HCl. A small amount of ferric iron (0.1 mg l^{-1}) was added and subsequently precipitated in hydroxide form following neutralisation with ammonia. By using such a small quantity of iron, only reduced (III, IV) plutonium species were co-precipitated, leaving oxidised (V,VI) species in solution. The ferric hydroxide precipitate was collected by filtration and retained for the analysis of the reduced fraction. Following reacidification of the sample and a further addition of Fe^{3+}, reduction of the oxidised species of plutonium was accomplished by the addition of appropriate reducing agents prior to precipitation.

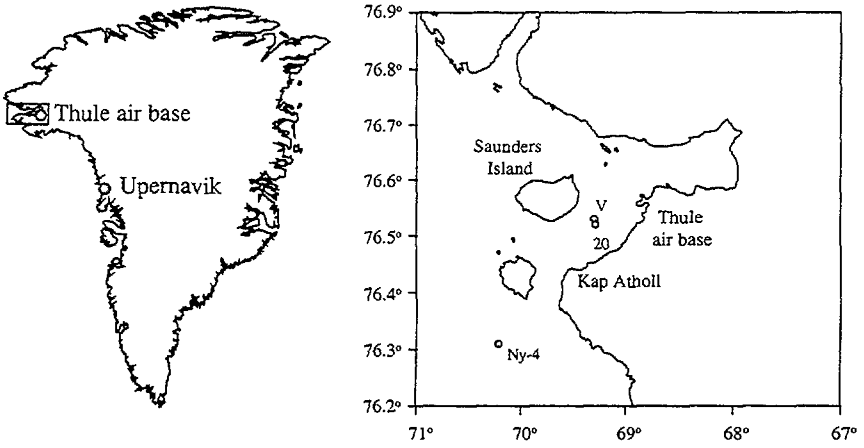

FIG. 1. Locations at which Pu chemical speciation analyses were carried out (Thule'97 expedition).

Plutonium was recovered from both fractions (precipitates) using routine radiochemical separation techniques based on selective sorption on ion-exchange resins, followed by electrodeposition onto polished stainless-steel discs. The concentration of ^{239,240}Pu in each fraction was determined by high-resolution alpha-spectrometry. Efficient separation of the two species was achieved, with cross-overs of less than ~6% in all cases. The resulting data are given in Table 1.

TABLE I. OXIDATION STATE DISTRIBUTION OF ^{239,240}Pu IN SEA WATER SAMPLED OFF THE NW COAST OF GREENLAND, AUGUST 1997. UNCERTAINTIES ARE GIVEN TO ±1σ

Location	Station depth (m)	Depth (m)	%^{239,240}Pu(V,VI) in filtrate	^{239,240}Pu (total) (mBq m^{-3})
Thule:				
Stn Ny-4 (76°18'N, 70°13'W)	290	2	75 ± 8	5.8 ± 0.5
		280	68 ± 5	10.8 ± 0.5
Stn V (76°32'N, 69°18'W)	187	2	67 ± 4	6.6 ± 0.3
		100	65 ± 4	11.2 ± 0.4
		177	59 ± 3	17.6 ± 1.0
Stn 20 (76°31'N, 69°17'W)		2	76 ± 7	9.3 ± 0.6
Upernavik:				
Stn 1(72°49'N, 56°12'W)		2	77 ± 10	7.5 ± 0.4

The data show that the bulk of the plutonium in the dissolved phase at all four stations was in an oxidised form, highlighting the oxygenated character of these cold shelf waters. Further, there appeared to be no difference between the proportion in oxidised form in surface water at stations close to the Thule accident site and that at a reference station remote from this site (i.e., Upernavik). However, there is a suggestion in the data of a slight decrease with depth in the proportion in an oxidised form. Overall, the percentage of oxidised ^{239,240}Pu in surface waters is similar to that observed by other workers in surface waters at lower latitudes [3, 4], suggesting that the underlying processes controlling plutonium speciation are insensitive to temperature over the range 0–25°C.

Measurement of the ^{238}Pu/^{239,240}Pu activity ratio in the water column (dissolved phase) at Thule yielded a mean value of 0.053 ± 0.015 (n=7) which, being similar to the global fallout ratio at these latitudes of about 0.04, suggests that there is virtually no weapons-grade plutonium in the Thule water column at the present time. This is in contrast to the underlying sediments which, in previous studies [e.g., reference 5], were found to exhibit considerably lower ratios (0.01–0.02), characteristic of weapons-grade plutonium.

Acknowledgements

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THE USE OF ^{59}Ni, ^{99}Tc, AND ^{236}U TO MONITOR THE RELEASE OF RADIONUCLIDES FROM OBJECTS CONTAINING SPENT NUCLEAR FUEL DUMPED IN THE KARA SEA

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Between 1965 and 1981, five objects and six naval reactor pressure vessels (RPVs) from four former Soviet Union submarines and a special container from the icebreaker Lenin, all containing damaged spent nuclear fuel (SNF) were dumped in a variety of containments, at four sites in the Kara Sea.

The International Atomic Energy Agency initiated the International Arctic Seas Assessment Project (IASAP) to study the possible health and environmental effects from disposal of these objects. One outcome of the IASAP was an estimation of the radionuclide inventory and their release rates from these objects. A follow-on concern is the ability to detect the radionuclides released into the water column. The work reported here is the feasibility of using the long-lived radionuclides ^{59}Ni, ^{99}Tc, and ^{236}U encased within these objects, to monitor the breakdown of the containments due to corrosion.

TABLE I. DISPOSAL INFORMATION FOR THE OBJECTS CONTAINING SPENT NUCLEAR FUEL DUMPED IN THE KARA SEA.

Disposal site	Year of disposal	Factory number	Dumped object	Disposal coordinates	Disposal depth (m)
Abrosimov Fjord	1965	901	Reactor compartment	71°56.03'N 55° 18.15'E	20
		285	Reactor compartment	71° 56.03'N 55° 18.08'E	20
Tsivolka Fjord	1967	OK-150	Lenin fuel container	74° 26.10'N 58° 36.15'E	50
Novaya Zemlya Depression	1972	421	Reactor	72° 40'N 58° 10'E	300
Stepovoy Fjord	1981	601	Submarine	72° 31.25'N 55° 30.25'E	50

The inventories used in the calculations of the annual mass release of ^{59}Ni and ^{99}Tc are those reported by the IASAP Source Term Working Group (IAEA 1997) from the objects listed in Table I. Using the best estimateD discharge scenario, corrosion rates, and methodology of the IASAP Source Term Working Group models [1], the annual activity release (Bq/a) of ^{59}Ni, ^{99}Tc, and ^{236}U were determined for the five disposal sites over the estimated period of release. Conversion to annual mass release (g/a) of ^{59}Ni, ^{99}Tc, and ^{236}U was accomplished through the appropriate application of isotopic specific activity (Bq/g).

To estimate the concentration of a radionuclide released from a dumped object to seawater, we used a simple equation to predict the average near-field concentration of a radionuclide released from a seabed dumpsite into a diffusive ocean [2]. Then, the mass of a radionuclide present in a seawater sample is determined from the product of the radionuclide concentration and the volume of the sample.

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Accelerator Mass Spectrometry (AMS) detection of the long-lived actinide elements is expected to be at least 2-3 orders of magnitude more sensitive than classical radiometric counting methods. Preliminary studies on the feasibility and sensitivity of using AMS detection demonstrate that detection limits in the order of 10^5 atoms (or < 0 1 fg) are achievable [3].

Based on our predicted release rates and dispersion of radionuclides from the dumped objects into the near-field seawater, we have examined the feasibility of measuring ^{59}Ni, ^{99}Tc, and ^{236}U in the waters of the Kara Sea as a tool to monitor the breakdown of containments due to corrosion. The limits of detection for measurement of ^{59}Ni and ^{99}Tc by AMS are about 2-5 fg and 10-100 fg, respectively. The absolute detection efficiency for ^{236}U is similar to that of other long-lived actinides (10^5-10^6 atoms or 0.04-0.4 fg) although actual detection limits will depend on isobaric interferences from ^{235}U.

The AMS limits of detection have been compared against the estimated mass of ^{59}Ni, ^{99}Tc, and ^{236}U expected in a 100 l seawater sample collected at a distance of 1000 m from the dumped objects as a function of the release year through to the year 5000. Figure 1 shows the result for the ^{236}U. ^{59}Ni is estimated to be present in sufficient quantities to be measured throughout the release period at all five sites. For ^{99}Tc the mass contained in the sample from the area of the submarine 601 is estimated to be of a measurable quantity only at the lower limit of 10 fg and in all but the early release years. At all other sites, with the exception of the early release years from the objects 901, 285, and 421 and late release from the Lenin fuel container, ^{99}Tc is estimated to be present in sufficient quantities to be measured throughout the release period. For ^{236}U, from the seawater sample off submarine 601, it is estimated to be of a measurable quantity only after the year 3106. At all other sites however, the ^{236}U is estimated to be present in sufficient quantities to be measured throughout all but the early release years for 901, 285, & 421 and late release from the Lenin fuel container.

For samples collected a distance of 100 m from the dumped objects, the ^{59}Ni, ^{99}Tc, and ^{236}U mass is predicted to increase tenfold. In the case of samples collected from the area of the submarine number 601, the ^{99}Tc could become measurable at the upper limit of 100 fg and the ^{236}U could become measurable some 925 years earlier.

If AMS techniques for measurement of the long-lived radionuclides ^{59}Ni, ^{99}Tc, and ^{236}U achieve the detection limits we have considered, then measurement of these radionuclides encased within the objects containing SNF dumped into the Kara Sea is a valuable tool to monitor the breakdown of the containments due to corrosion. Seawater samples collected within 1000 m of the sites are predicted to yield measurable quantities of ^{59}Ni throughout virtually the entire release period. Whether the ^{99}Tc mass collected from the area of the submarine 601 is measurable depends on the range-in-detection limit. At the lower limit of 10 fg, ^{99}Tc is estimated to be present in sufficient quantities to be measured throughout most of the entire release period at all sites. At the upper limit of 100 fg, measurable quantities of ^{99}Tc mass are also predicted from the submarine 601, if the samples are collected 100 m from October 2, 1998the object. Disposal sites with the greatest relative release periods of measurable ^{236}U mass are those containing the units 901& 285 (Abrosimov Fjord), and unit 421 (Novaya Zemlya Depression) and the Lenin fuel container (Tsivolka Fjord). If samples are collected 100 m from the submarine number 601 (Stepovoy Fjord), measurable quantities of ^{236}U are predicted in the year 2181, some 925 years earlier.

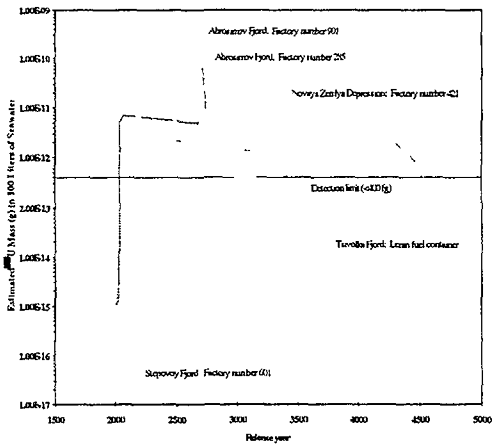
Figure 3. Comparison of Estimated ^{236}U Mass (g) in 100 Liters of Seawater from Various Disposal Sites in the Kara Sea versus Release Year

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IAEA-SM-354/10P

RADIOACTIVE CONTAMINATION OF THE SEAS WASHING THE TERRITORY OF RUSSIA (1961-1966)

XA9951943

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The territory of Russia is washed by 13 seas. These are the sea of Azov, the Black sea, the Caspian sea, the Baltic sea, the White sea, the Barents sea, the Kara sea, the Laptev sea, the East-Siberian sea , Chukchi sea , the Bering sea, the sea of Okhotsk and the sea of Japan.

Regular monitoring of the radioactive contamination of the seas was started in 1961 by the Hydrometeorological service of USSR. Initially, the data consisted of total beta activity and since 1962-1963 monitoring of the Sr-90 content was conducted as well. Results of the observations of strontium-90 in the seas washing the territory of Russia in the period of 1963-1968 were presented by Chumichev in [1]. Data from that work and data for 1988-1991,1995-1996 [2,3,4] are included in Table I.

In the period 1967-1980 detailed surveys were performed of the Baltic sea , the Black sea and the Caspian sea with the aim to estimate the inventory of radionuclides in these seas and evaluate the contribution of different contamination sources. Based on experimental studies, estimation was made of the inflow of strontium-90,cesium-137 and tritium from the atmosphere and with the river run-off to the Baltic sea, the Black sea and Caspian sea .These estimates were compared with the inventory of these radionuclides in the water and bottom sediments of the above seas. The comparison has revealed that the main source of sea contamination was global radioactive depositions due to atmospheric nuclear tests carried out in 1945-1962 [5,6,7]. The exception was the inventory of strontium-90 in the Black sea which was 1.45 PBq for the sea as a whole and 3.4 kBq m^2 for a unit area and was two times higher the value of the inventory which could be associated with global radioactive depositions. Table 2 shows data on the distribution of strontium-90 inventory in the Black sea in 1977. Unfortunately, up to date the source of additional inflow of strontium-90 to the Black sea has not been identified.[8].

The results of studies of sea contamination due to global radioactive depositions became the basis for estimating the actual contribution to radioactive contamination of different industrial sources including disposal of solid and liquid radioactive waste in the Arctic and Far East seas washing the territory of Russia. The most significant industrial contamination sources for the seas washing Russia were: transboundary transport of cesium-137 from the Irish sea with the sea currents to the Baltic sea, Barents sea, the White and Kara seas; atmospheric depositions of cesium-137 after the Chernobyl accident on 26 April 1986 and the delivery of strontium-90 with the water of the Ob' river to the Kara sea.

From 1970 to 1990 within scientific programs in the former USSR and Russia studies of radioactive contamination were carried out in the radioactive waste disposal sites in the Barents and Kara seas and the sea of Japan. The discharge of liquid and solid radioactive waste in these seas was realized in designated areas in compliance with special sanitary standards providing that sea contamination levels should not lead to restrictions in sea food consumption [9]. In the period 1984-1990 the maximum water contamination levels in the areas of liquid waste discharge to the Barents sea measured in the first hour after the discharge did not exceed 2 % of the established standards for strontium-90; 0.6% for cesium-137 and less than 0.1% for cesium-134, cobalt-60, europium-152,154. In the areas of disposal of solid radioactive waste, as demonstrated by Russian-Norwegian and Russian-Japanese cruises in 1992-1995, the impact on the radiation situation was reported only in the bays of the Novaya Zemlya in the immediate proximity of the disposal sites [10].

The analysis of experimental data obtained with the purpose of estimating the radiation situation has made possible considering radioactive isotopes in the sea environment as tracers for estimation of velocity of water mass transport by currents, vertical exchange and sedimentation rate in bottom sediments and identification of areas of propagation of river water in the seas. This avenue holds a major potential for the specialists involved in sea monitoring together with those working in oceanography.

TABLE I. MEAN ANNUAL CONCENTRATIONS OF STRONTIUM-90 IN THE SURFACE SEA WATER IN 1963-1996 (Bq m ^{3})

Sea	Year											
	1963	1964	1965	1966	1967	1968	1988	1989	1990	1991	1995	1996
Azov							41	37	32	31	24	21
Baltic		59	41	41	37	30	19	20	20	17		
Barents	24	20	22	17	9	11	7	6	7.7	6	3,5	3.6
White	55	31	22	22	20	18	10	11	9.2	9.0	4,6	4.3
Caspian												
north part					92	110	20	21	15	13		
middle and south part	37	37	22	26	22	18	14	13		12		
sea of Okhotsk		19	15	12	10	14	5,5	6.2	3.6	3.7	1.8	2.1
sea of Japan		24	14	10	10	7.4	7,8	7	6.2	3.7	2.6	2.3
Black							24	24				

TABLE II INVENTORY OF SR-90 IN THE BLACK SEA WATER IN 1977

Water layer,m	Water volume, 10^{3} sq.m	Average concentration Bq/m^{3}	Inventory, 10^{14} Bq	Part of the total inventory, %
0-100	37	19.05	7.05	48.52
100-300	62	8.05	5.0	34.41
300-500	60	0.97	0.58	3.99
500-1000	141	0.65	0.92	6.33
1000-1500	127	0.45	0.57	3.92
1500-2000	114	0.36	0.41	2.82
Total	541		14.53 (39,27 $\times 10^{3}$ Ci)	99.99

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IAEA-SM-354/11P

THE IAEA INVENTORY DATABASES RELATED TO RADIOACTIVE MATERIAL ENTERING THE MARINE ENVIRONMENT

XA9951944

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Contracting Parties to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter (LC 1972) have requested the IAEA to develop an inventory of radioactive material entering the marine environment from all sources. The rationale for developing and maintaining the inventory is related to its use as an information base with which the impact of radionuclides entering the marine environment from different sources can be assessed and compared.

Five anthropogenic sources of radionuclides entering the marine environment can be identified. These sources are: radioactive waste disposal at sea; accidents and losses at sea involving radioactive material; discharge of low level liquid effluents from land-based nuclear facilities; the fallout from nuclear weapons testing; and accidental releases from land-based nuclear facilities. The first two of these sources are most closely related to the objective of the LC 1972 and its request to the IAEA. This paper deals with the Agency's work on developing a database on radioactive material entering the marine environment from these two sources. The database has the acronym RAMEM (RAdioactive Material Entering the Marine Environment). It includes two modules: inventory of radioactive waste disposal at sea and inventory of accidents and losses at sea involving radioactive material.

The database module on sea disposal of packaged radioactive waste includes relevant disposal data such as total volume and activity of disposed waste, the State responsible for disposal, waste type (solid objects, solidified or liquid waste, reactor vessel with or without fuel), matrix type (concrete, bitumen, polymer etc.), containers (type, weight, number etc.) and geographical coordinates and depth of the disposal site. The first output of the inventory, IAEA - TECDOC - 588 [1] published in 1991, included disposal operations reported by 12 countries. This inventory has recently been updated to include information provided by the Russian Federation on disposal operations carried out by the former Soviet Union and subsequently the Russian Federation and some additional disposal information provided by Sweden and the UK. These information on sea disposal operations has been confirmed by the States involved. Dumping operations have been carried out in the Atlantic, Pacific and Arctic Oceans. The dumping sites and respective total activities are presented in Fig. 1. The distribution of disposed activities among the countries involved are summarized as follows:

Total activity disposed by 14 countries (1946-1993)		85 PBq (2.3 MCi)
Atlantic Ocean	-	45.26 PBq (53.2% - nine countries)
Arctic Ocean	-	38.37 PBq.(45.1% - former Soviet Union)
Pacific Ocean	-	1.44 PBq (1.7% - four countries)

The radioactive waste types and activity in the disposed wastes are summarized as follows:

Low level solid waste	-	45.45 PBq [53.42%]
Low level liquid waste	-	1.22 PBq [1.44%]
Reactors with spent nuclear fuel	-	36.88 PBq [43.34%]
Reactors without spent nuclear fuel	-	1.53 PBq [1.80%]

The module of the database on accidents and losses contains the information on date of the accident or loss, material involved such as vessels, aeroplanes, satellites, sealed sources etc., geographical location and depth of loss, a brief description of the source involved, whether recovered, whether monitoring was carried out, and whether any activity was released to the environment. All accidents and losses included in the database are either officially notified or confirmed by the States involved or based on authoritative information. The data is categorized into: (a) accidents involving nuclear powered submarine, 9 out of which 7 was confirmed (5 accidents resulted in loss of submarine containing about 25 PBq of activity at the time of loss, nuclear weapons were carried in 3 submarines); (b) accidents involving nuclear weapons, 17 accidents out of which 9 have been confirmed (14 accidents resulted in loss, two recovered and one partially recovered); (c) accidents involving energy sources used in spacecraft, satellites, and deep sea acoustic signal transmitters, 5 accidents resulting in the loss of 4 satellites and 1 spacecraft (total estimated activity was 4.7 PBq); (d) one accident involving RTG powered light house during transportation by helicopter with total activity of 13 PBq - recovery was not successful; (e) accidents during marine transport of radioactive material, 3 accidents involving about 334 TBq activity without any reported release of activity; and (f) accidents involving sealed radioactive sources primarily been used in the offshore oil and gas drilling industry, 156 incidents reported by 9 countries with the loss of sources predominantly in the drill holes with activity in the range of 50 to 3700 GBq per source, sources were recovered in 10 other incidents.

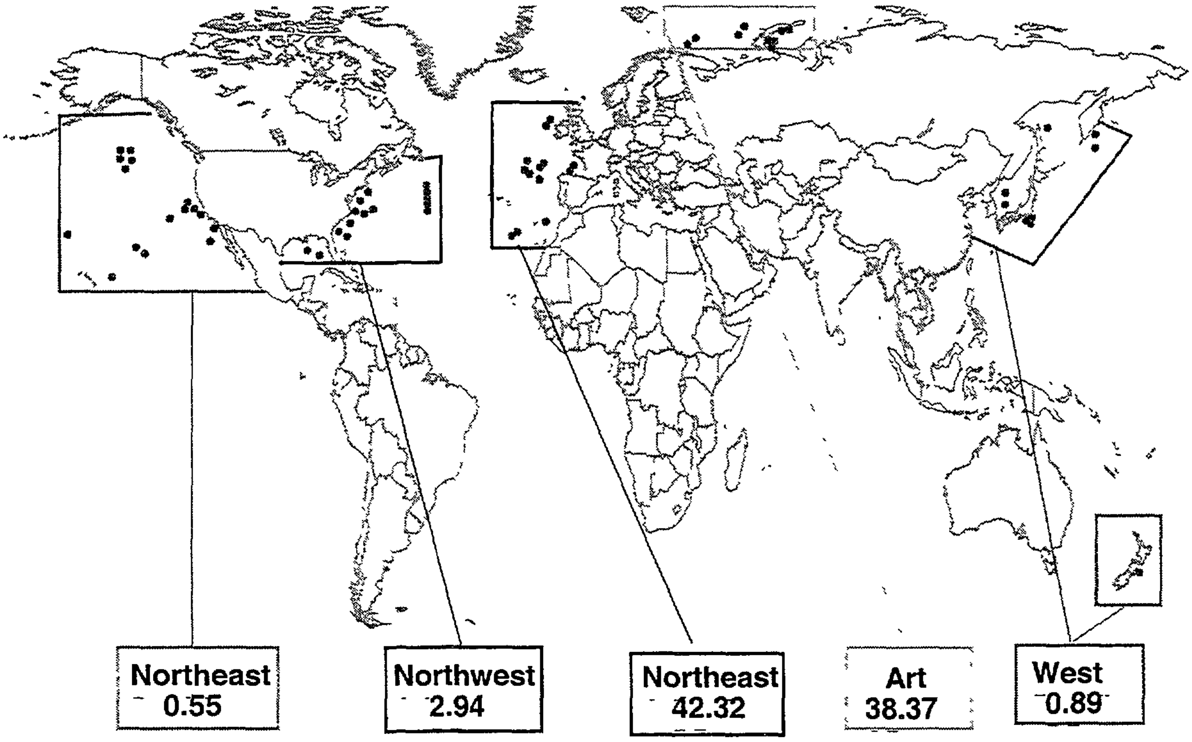

FIG. 1. Disposal at sea of radioactive waste - world wide.

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RADIOACTIVE CESIUM, COBALT AND PLUTONIUM IN BIOTA, ALGAE AND SEDIMENTS IN THE NONRESTRICTED AREAS OF THE RUSSIAN ARCTIC SEAS

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Biota, macroalgae and sediment samples were collected during scientific expeditions organized by the Murmansk Marine Biological Institute (MMBI) during 1993 - 1996 in the Barents, Petshora, Kara, Laptev and White seas and in the Kola Bay. The purpose of the expeditions was to study the levels of radioactive pollution in the Russian arctic seas.

^{137}Cs levels were low in all the biota samples, 0.3 - 1 Bq/kg f. w. in fish and Greenland seal pups, and <0.3 - 6 in sea birds and in 200 benthic species [1]. Slightly higher concentrations, 2 - 4 Bq/kg d.w. were found only in algae samples in the White Sea and in some closed bays along the Kola Peninsula coast. The plutonium isotope concentrations were low in all the biota samples, in the flesh of fish ^{239,240}Pu <2 mBq/kg, exept for 7.8 Bq/kg in ray, and in sea birds and seal pups <1 - <8 mBq/kg f.w.

Slightly higher levels were found only in brittle star, ^{239,240}Pu 14 - 20 mBq/kg f.w, ^{238}Pu <10 mBq/kg. In all the other biota samples the ^{238}Pu concentrations were <1 mBq/kg. The ^{239,240}Pu concentrations of algae varied 0.02 - 0.23 Bq/kg d.w., except for red algae from Kolguev Island 0.28 Bq/kg d.w. All the ^{238}Pu concentrations were <0.01 Bq/kg.

In the surface sediments the ^{137}Cs concentrations, Bq/kg d.w. *(Fig. 1),* in most cases varied 0.2 - 20 Bq/kg d.w. and the concentrations calculated per quare metre 2 - 150 Bq/m^2. Higher levels of 20 - 81 Bq/kg and 150 - 580 Bq/m^2 were measured only in the White Sea, and in the estuaries of the rivers Dvina, Ob and Yenisey. The ^{239,240}Pu concentrations (Fig. 2) varied 0.14 - 4.4 Bq/kg and 2.5 - 25 Bq/m^2. A sligtly higher concentration of 46 Bq/m^2 was found at only one sampling site south of Novaya Zemlya.

The plutonium activity ratio, ^{238}Pu/^{239,240}Pu varied 0.023 - 0.083, except at four locations in the Kola Bay [2] and at one location in the White Sea [3]. In the Kola Bay the increased ratio (0.10 - 0.12), indicates a certain amount of fresh release from the nuclear icebreaker facility or from the storage vessels in front of Atomflot, or from the military nuclear submarine bases. The origin of the increased ratio in the White Sea is unknown, but one dumping site for liquid radioactive waste has been reported by Yablokov *et all.* [4] in the vicinity of this site.

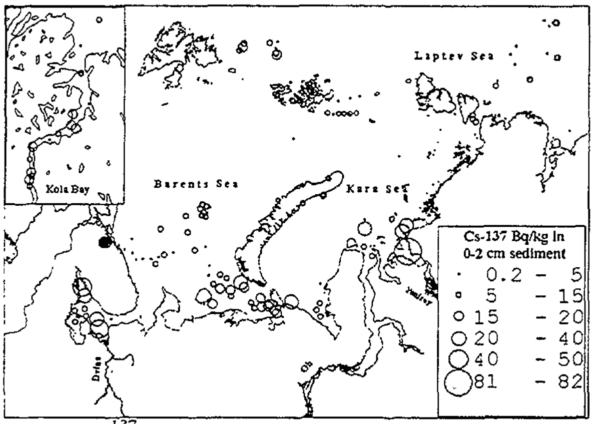

FIG. 1. ^{137}Cs, Bq/kg, in surface sediments

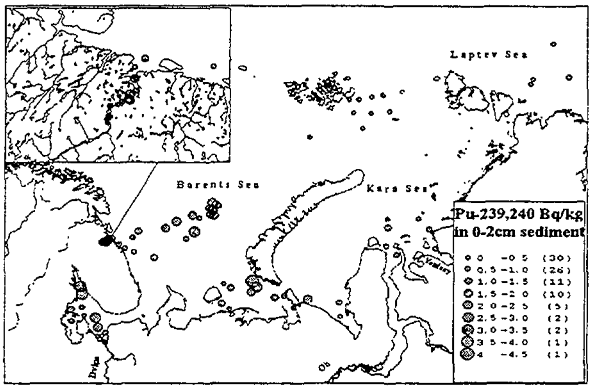

FIG. 2. ^{239,240}Pu, Bq/ kg, in surface sediments

The effect of riverine transport on the cesium and plutonium concentrations in the estuary sediments has been studied by calculating the ratio ^{137}Cs/^{239,240}Pu. The highest ratios, 105 - 110, were obtained in the estuaries of the River Dvina and River Yenisey (Fig. 3.), indicating an excess of radiocesium input from the large catchment areas. The total ^{137}Cs load of the 0 - 20 cm surface layer was calculated to be about 5800 Bq/ m^2 in River Dvina and about 5200 Bq/m^2 in River Yenisey estuary. Increased ratios of 20 - 40 were also found in the southern part of Kola Bay and outside the inlet of the River Ob. A ratio of 80 was noticed inside the archipelago of Franz Josephs Land. The lowest ratios, 2.3 - 5.3, were measured in the open part of the Barents Sea.

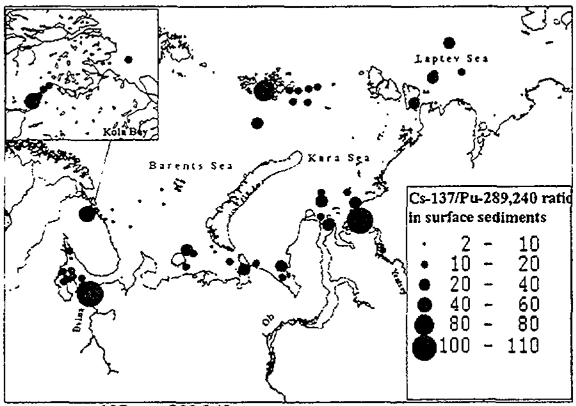

FIG. 3. $^{137}Cs/^{239,240}Pu$ ratio in surface sediments

The activation product ^{60}Co was detected in benthic and algae samples from near a dumping site [4] in the Barents Sea to the north-east of Kolguev Island, in the Kola Bay near the Polarnyi nuclear submarine base, and in all sediment sampling locations between the nuclear icebreaker base Atomflot and the Barents Sea [2]. ^{60}Co was also detected in the River Yenisey estuary sediment from the Kara Sea and in the Kandalaksh Bay (White Sea) [3].

The measured radioactivity levels were low compared to all the potential pollution sources in the Russian Arctic seas. In most cases the radioactivity levels in the nonrestricted sea areas originate from nuclear weapons testing and the Chernobyl accident. Increased radiocesium levels in sediments are caused by riverine transport. However, presence of ^{60}Co and increased $^{238}Pu/^{239,240}Pu$ ratios also indicate some fresh contamination and release, especially in the Kola Bay.

Acknowledgement

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IAEA-SM-354/15P

DOES BENTHIC COMMUNITY STRUCTURE INFLUENCE RADIONUCLIDE INCORPORATION INTO THE FOOD WEB?

XA9951946

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Since publication of the White Book on the dumping of nuclear reactors and discharges of radioactive materials into shallow Arctic seas [6], several risk assessments addressing current and future impacts from the wastes have been completed [5,1,4]. These studies convincingly demonstrate that with the exception of a few local "hot spots," radioactivity levels have not significantly increased in the Arctic and doses to humans from key nuclear waste-related radionuclides are currently below acceptable levels. Furthermore, major failures of containment systems for the dumped nuclear reactors are not predicted to occur for perhaps another thousand years. It is therefore appropriate to revisit debates surrounding key difficulties encountered in conducting risk assessments for humans and biological resources in the Arctic.

One important aspect of the risk assessment process is the prediction of radionuclide transfer into and through the marine food web. The current class of risk assessments are based on a simplified two step approach, that is, exposure of fish to radioactivity and subsequent consumption by humans. Discussions have focused on predicting the transfer of radionuclides from abiotic components of the marine environment (water and particulate matter) into the food web, (e.g. the bioconcentration factor approach). This approach was chosen out of necessity because there is inadequate information on biological communities in Arctic seas. Many questions remain concerning the role of biological community structure in controlling the transfer of radionuclides from low to high trophic levels within the Arctic food web. For example, how do inter-relationships between species (e.g. competition, predator-prey interactions, life-history variations) and other ecological processes affecting community structure (e.g. recruitment), influence the mobilization and transfer of contaminants? We explore one facet of the food-web issue. Namely, how does benthic community structure influence radionuclide incorporation into the food web?

Benthic biomass and species density data were determined for field samples collected in 1993 and 1994 as part of the KAREX program (see Dahle et al., this symposium). These data provide a characterization of the Arctic benthic community structure within different regions of the Kara Sea. Benthic data were grouped into four geographic locations, Ob/Yenisey delta (EST) Eastern Kara Sea (NKS), Western Kara Sea (WKS) and the Novaya Zemlya Trough (NZT). Radionuclide concentrations in seawater for each region were derived from model results of a compartmental model developed to perform radionuclide risk assessments in the Kara Sea [2]. The model was used to simulate releases from the Ob River system of 1 TBq of caesium. After three simulation years, radionuclide concentrations in the Kara Sea were noted. We then modeled the uptake of caesium from water to benthic organisms assuming equilibrium partitioning of radioactivity. Using estimates of radionuclide bioconcentration factors [3,1], radionuclide uptake was calculated in each of the four regions for four major phyla (Mollusca, Annelida, Crustacea and Echinodermata).

In terms of biomass, the benthos was generally dominated by Mollusca and Annelida. In the northern region (NKS), there is also a high contribution (69.5 g/m^2) from organisms that are not classified into the above four major phyla represented in the Kara Sea. The contribution of this diverse mixture of species to bioaccumulation and transfer of caesium through the food web could not be estimated. Modeling the discharge of caesium from the Ob river system resulted in variations in seawater radionuclide concentrations ranging over several orders of magnitude. It is not surprising that over short-timescales (e.g. less than few years), the first-order control on radionuclide bioconcentration to benthic organisms is due to proximity to the discharge source. For the Kara Sea simulations, radionuclide bioconcentration levels are highest in the estuary (EST), but the biomass (wet weight in grams/m^2) there is lowest. Low biomass near the discharge source helps limit the potential transfer of radionuclides through the food web. Biouptake within individual phyla varied among sites in accordance with radionuclide concentrations in seawater, with one exception. Low biomass limits biouptake to Crustacea in NZT.

The Mollusca, which are efficient bioaccumulator organisms, are prominent in the benthos and thus is an important starting point for bioaccumulation through the Kara Sea food web. Walrus are known to harvest some species of Mollusca providing an efficient and direct pathway for bioaccumulation to higher trophic levels. The Annelida also contribute significantly to biomass distributions within the Kara Sea. Although less is known about specific predator species, Annelida consumption by bottom dwelling fish, and in some cases directly by seals is another pathway in the food web which should be carefully studied for the Kara Sea. We have modelled patterns of radionuclide uptake from the abiotic environment into the food web of the Kara Sea. The approach, provides a first-order glimpse at how organisms occupying the bottom of the food web might set the stage and thereby influence radionuclide transfers to higher trophic levels.

TABLE I. CAESIUM BIOUPTAKE TO BIOTA: TOTAL BIOACCUMULATION IN Bq/m^2 OF SEDIMENT SURFACE. THE PERCENTAGE OF THE TOTAL IS GIVEN FOR EACH PHYLA.

	EST	NKS	WKS	NZT
Total Bioaccumulation	2,0E-04	1,1E-07	3,6E-06	9,1E-07
Annelida	23,7 %	67,0 %	17,7 %	40,6 %
Crustacea	17,3 %	2,3 %	18,5 %	0,6 %
Echinodermata	0,3 %	1,3 %	1,1 %	0,4 %
Mollusca	58,8 %	29,4 %	62,6 %	58,4 %
Biomass (wet wt. g/m^2)	135	219	244	158

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PEUPLEMENT DES SABLES FINS DES COTES ALGERIENNES : AMPHIPODES ET POLLUTION

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Les investigations menées depuis un certain nombre d'années au niveau des baies (Alger, Bou - Ismail, Fetzara) et des golfes (Arzew, Bejaia Jijel) de la cote algérienne, ont permis de localiser, identifier et caractériser le peuplement des sables fins des secteurs prospectés. Ce peuplement occupe les faibles profondeurs (0 a 20-25 m), ils forment une bande c6tidre localisée au fond des baies et golfes, lieu d'aboutissement des rejets d'eaux usées des grandes villes et/ou des pôles industriels c6tiers ; les impacts de ces rejets sur le peuplement des sables fins permettent d'évaluer les flux de pollution affectant ces fonds. Dans ce sens, l'analyse des richesses spécifique et numérique du peuplement , plus particulièrement de l'un de ses compartiments, les Amphipodes, est un outil fort appréciable.

- **Golfe d'Arzew** : Le littoral est fortement urbanisé et industrialisé : nombreuses villes c6tidres, deux ports, l'un constitue le premier port algérien d'exportation d'hydrocarbures, premier pole industriel algérien (pétrochimie, liquéfaction de gaz naturel)
- **Baie de Bou-Ismail** : La c6te est très faiblement urbanisée, et non industrialise, région essentiellement a vocation agricole.
- **Baie d'Alger :** Le littoral de la baie et la région attenant sont des zones fortement urbanisées et industrialisées : 12 % de la population soit environ 3,5 M. d'habitants et 22 % des activités industrielles algériennes. Les eaux usées sent traînées vers la mer par de très nombreux émissaires et deux oueds. Dans cette baie, il existe un gradient de pollution décroissant d'ouest en Est : le secteur Ouest (Station I) est le plus pollué; le secteur Est (Station 4) le mains pollué, et le secteur Centre, en situation intermédiaire (stations 2 et 3). La baie d'Alger de la c6te algérienne est le secteur le plus pollue.
- **Golfe de Bejaia** : Sur son littoral sont implante les une ville, Bejaia, et une zone industrielle relativement importantes.; Cependant le port de Bejaia est un des premiers pour l'exportation du pétrole brut.
- **Golfe de Jijel et baie de Fetzara :** Leur littoral est très faiblement urbanisé, et non industrialisé, constituant ainsi des régions naturelles par excellence.

Pour chacun des secteurs concernes, il a été évalué la richesse spécifique des Amphipodes, et leur pourcentage par rapport a la diversité totale du peuplement, la dominance cumulée des Amphipodes classés par espèces principales, la dominance moyenne de l'ensemble des Amphipodes (tableau ci-dessous), et leur fréquence dans le peuplement.

- **Arzew** : Aucun Amphipode ne figure parmi les principales espèces ; *Hippomedon denticulatus, Ampelisca sarsi,* les plus fréquentes ne sont que des espèces peu communes. Baie de Bou-Ismail *: Urothoe grimaldii, U poseidonis, U. brevicornis, Ampelisca brevicornis* sont les espèces principales du peuplement. Dans le peuplement on dénombre deux espèces communes : *Ampelisca brevicornis* , *Lembos spiniventris* et sept peu communes: *Siphonoecetes dellavallei ; Urothod grimaldi, U poseidonis, Ampelisca diadema, A. sarsi, Lembos angularis, Phtisica marina.* Presque le quart des individus du peuplement sont des Amphipodes.

- **Baie d'Alger** : Selon le secteur, la représentativité spécifique et numérique des Amphipodes est différente. Elle augmente du secteur le plus pollué vers le secteur le mains pollué . Ces Amphipodes constituent 9,01 (station 1) a 14,94 % (station 4) de la diversité fatale, et leur dominance moyenne fluctue entre 1,29 (station 1) et 3,54 % (station 3). Il n'y a aucun Amphipode des espèces principales aux stations 1 et 2, tandis qu'aux stations on observe 3 et 4, *Pariambus typicus f armata* qui est une espèce principale très commune , et espèce commune aux stations 1 et 2. *Ampelisca spinipes* est espèce commune a la station 3 et a la station 4 associée a d'autres espèces communes : *Ampelisca sarsi, Urothoe brevicornis, Leucothoe lilljeborgi, Bathyporeia guilliamsoniana.* La diversité , l'abondance, la fréquence des Amphipodes aux stations sont étroitement liées au degré de pollution les affectant.
- **Golfe de Bejaia :** *Urothoe poseidonis , U. puichella, Ampelisca brevicornis, A. diadema, Aora gracilis* figurent parmi les espèces principales. Les trois premières sont des espèces constantes auxquelles s'ajoutent les espèces communes :*Ampelisca diadema, A. pseudospinimana, Aora gracilis, Harpinia antennaria, Perioculodes longimanus.*
- **Golfe de Jijel** : La moitié des espèces principales sont des Amphipodes : *Ampelisca brevicornis* (espèces leader du peuplement), *A. spinipes, A. diadema , A. sarsi, Lembos spiniventris, Urothoe poseidonis, U brevicornis.* Ces principales espèces très communes rassemblent la moitié des effectifs du peuplement, tandis que l'ensemble des Amphipodes, un peu plus de la moitié du peuplement total..
- **Baie de Fetzara** : *Siphonoecetes dellavallei* (espèce leader), *Urothod grimaldii* et *U pulchella, Ampelisca sarsi,* sont des espèces principales. *U grimaldii* est espèce constante, tandis que *Siphonoecetes dellavallei* et *Ampelisca brevicornis* sont des .espèces très communes, Perioculodes longimanus étant une espèce commune. Les Amphipodes constituent un peu plus du quart des effectifs du peuplement.

TABLEAU I. RESULTATS

	Nombres d'espèces	*% Diversité Totale*	*Dominance espèces principales*	*Dominance Amphipodes*
Arzew	27	16.46	0	6.69
Bou-Ismail	39	17.81	11.49	21.5
Alger: Station1	20	9.01	0	2.38
Station 2	19	9.94	0	1.29
Station 3	21	10.77	2.27	3.54
Station 4	36	14.94	1.34	3.35
Bejaia	19	12.10	12.63	18.07
Jijel	30	20.98	49.98	52.57
Fetzara	21	15.67	20.27	27.92

La comparaison de la diversité, de la dominance numérique et de la fréquence des Amphipodes au sein de chacun des peuplements de SF des baies et golfes étudies, révèle une relation étroite entre ces indices et le degré de pollution du milieu. La disparition, la raréfaction ou la grande diversité des Amphipodes sont autant d'informations sur la qualité du milieu. Cette sensibilité des Amphipodes a la pollution déjà mentionnée par certains auteurs (1,2&3), fait d'eux d'excellents indicateurs biologiques ; leur mode de reproduction direct et l'insularité géographique de leur population (2) renforcent leur caractère d'indicateurs biologiques.

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^{210}Po UPTAKE BY ZOOPLANKTON DURING A ONE YEAR CYCLE IN RELATION TO TROPHIC CONDITIONS IN MONACO BAY.

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Former evidence [1] showed that in oligotrophic waters in French Polynesia there is an inverse correlation between zooplankton biomass and zooplankton ^{210}Po concentration. To study the same phenomenon in a more seasonal environment, , monthly samples of zooplankton, water, fecal pellets, and particulate organic matter were obtained in Monaco monthly and analyzed for ^{210}Po content. Trophic conditions were obtained by analyzing the biochemical composition of particulate organic matter (POM) at 0, 20 and 50 m depths. a constant input of ^{210}Po, from the decay of ^{210}Pb and ^{222}Ra Was assumed. But the mechanism by which ^{210}Po is accumulated in zooplankton seems to be more complicated than previously expected.

Organic samples were digested with nitric acid hydrochloric acid and hydrogen peroxide, adding of ^{209}Po as tracer, [2]. For water samples, the same procedure was utilized, with minor adaptations. For protein carbohydrates and lipids determination, the methods are described elsewhere [3,4].

Zooplankton biomass showed a typical spring "bloom" during May (see Fig. 1), which was preceded by a maintained high POM (the sum of proteins plus lipids plus carbohydrates) which started at the end of March and receded in May. In August there was another "bloom" but it did not sustained an increase of zooplankton biomass. High POM values were found also during October and November but zooplankton biomass was peristently low.

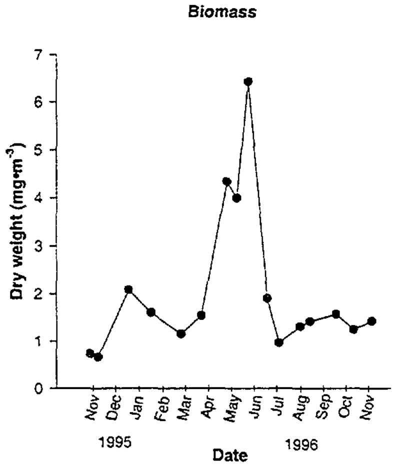

FIG 1. Zooplankton biomass in Monaco Bay.

Total zooplankton ^{210}Po concentration and water ^{210}Po concentration showed a opposite trend, but they were not significantly correlated. The highest ^{210}Po concentration in zooplankton coincided with the lowest ^{210}Po concentration in water (see Fig. 2), and also with the lowest POM concentration (see Fig. 3). No correlation was found between ^{210}Po zooplankton concentration and zooplankton biomass, for the whole sampling period. However, zooplankton biomass in Monaco, was never as low as in French Polynesia.

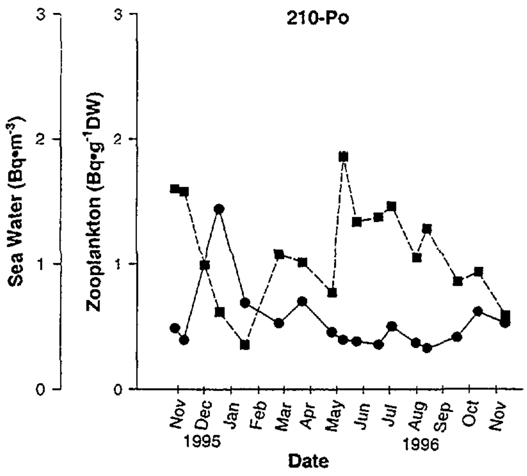

FIG. 2. ^{210}Po concentration in water and zooplankton in Monaco bay

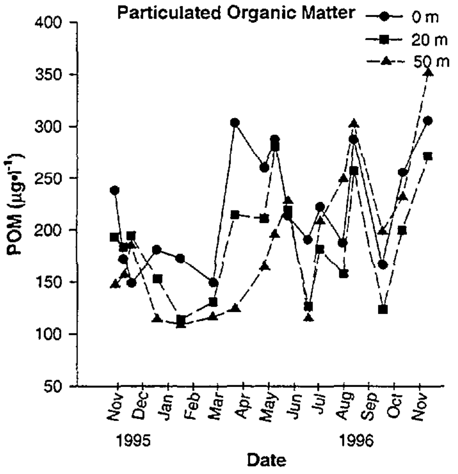

FIG. 3. POM in Monaco Bay

Zooplankton fractions of different sizes showed a significant difference for ^{210}Po concentration. Different taxonomic groups of zooplakton also exhibited quite different values. It is apparently important to consider taxonomic composition and size of the individuals to understand the mechanism of bioaccumulation, and how ^{210}Po is "shared" by the different components of the "system": water, zooplankton, fecal pellets, particulate matter (organic or inorganic) and phytoplankton, in a highly seasonal environment like the Mediterranean Sea.

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DISTRIBUTION OF HEAVY METALS IN SEDIMENTS OF THE VENICE LAGOON: THE ROLE OF THE INDUSTRIAL AREA

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The Venice Lagoon has been heavily polluted both from diffuse and direct sources. It has been recently established that the atmospheric delivery of contaminants to the lagoon can be very significant in zones far from direct sources, but the influence of the industrial area of Porto Marghera, though widely recognized, has not been entirely described and quantified. In order to assess the temporal and spatial variability of metal pollution, and to better understand the contribution of the industrial channels as sources of contaminants, in May 1996 we sampled 18 stations in the lagoon and 9 in the channels of the industrial area of Porto Marghera. At each site a short core, 10 cm long, was taken and immediately extruded to obtain 4 slices 2-2.5 cm thick. Sediment samples have been analysed for As, Cd, Pb, and Zn after acid extraction. Based on this approach we obtained information on the very recent sediment record: assuming accumulation rates of 0.3-0.4 cm y^{-1} the top 10 cm represent 25-30 years and each section 6-7.5 years. The results relative to surficial samples are summarized in the Table. Zn is the metal which shows the highest concentrations in lagoon sediments.

TABLE I. CONCENTRATION INTERVALS OF METALS IN THE SURFICIAL SAMPLES. BACKGROUND VALUES ARE FROM ORIO AND DONAZZOLO (1987).

Metal	Channels (μg/g)	Lagoon (μg/g)	Background (μg/g)
As	5 - 120	5 - 25	-
Cd	0.3 - 70	0.2 - 5	< 1
Pb	21 - 929	38 - 114	< 25
Zn	113 - 8295	101 - 1115	< 70

Maximum values, are relative to the sample taken from the Canale Industriale Nord which is presently the most important source of pollutants to both the Canale dei Petroli and the lagoon. This is confirmed by metal distributions in lagoon sediments: the highest concentrations have been found in sediments close to the mainland, in a wedge-shaped area located between the Canale Vittorio Emanuele III and the Isola delle Tresse. The comparison of metal distributions in sediments at various levels shows the evolution of the inputs. The patterns suggest that the heavily polluted areas are reducing in size but the influence of the materials stored in the the Canale Industriale Nord has increased through time, and is presently the most important. Metal distributions are also discussed on the basis of grain size composition of sediments and water circulation patterns. Despite many previous studies, these results for the first time clearly point out the potentially most dangerous source of pollutants within the lagoon system.

REPONSE QUANTITATIVE DES COMMUNAUTES DE NEMATODES SOUMISES A L'INSTABILITE SPATIO-TEMPORELLE D'UNE LAGUNE POLLUEE : LE LAC SUD DE TUNIS

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Le lac sud de Tunis, soumis aux flux continus de rejets organiques, domestiques et industriels, est sujet à une forte eutrophisation. Ce phénomène qui s'accentue en été s'accompagne de la mort des macroalgues et du dégagement d'odeurs nauséabondes, des eaux rouges y apparaissant sporadiquement.

Des prélèvements saisonniers de nématofaune sont réalisés à partir de 10 stations d'échantillonnage de mars 1996 à décembre 1996 afin d'une part de connaître la réponse des nématodes à la pollution organique qui caractérise actuellement le plan d'eau et d'autre part d'avoir un état référentiel de cet écosystème avant les grands travaux d'assainissement et d'aménagement qui y sont projetés (Fig. 1). L'instabilité physico-chimique du lac sud se répercute sur toutes les données quantitatives des communautés de nématodes aussi bien à l'échelle spatiale que temporelle

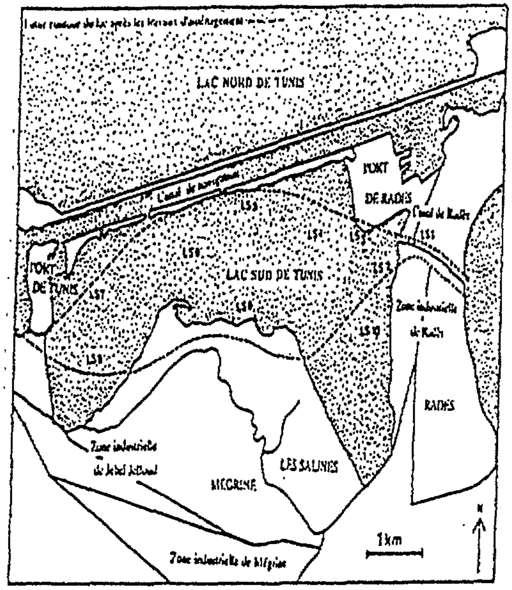


FIG. 1 Localisation des stations

C'est ainsi que les prélèvements, toutes stations confondues, montrent une chute considérable des densités durant la saison estivale, la moyenne saisonnière n'étant que de 12 individus. 10 cm^{-2} contre une moyenne maximale de 591 individus. 10 cm^{-2} relevée en hiver, cette grande abondance des nématodes pendant la saison hivernale ayant été relevée dans d'autres biotopes (1) (2). Des densités moyennes intermédiaires, respectivement égales à 266 individus. 10 cm^{-2} et 300 individus. 10 cm^{-2} sont enregistrées au printemps et en automne (Fig 2). L'étude statistique réalisée par le biais du test de Student confirme ce résultat, les effectifs estivaux apparaissant très significativement plus faibles que ceux relevés aux autres saisons. De la même façon, la biomasse totale moyenne des peuplements nématologiques, toutes stations confondues, fluctue entre un minimum estival de 0.019 mg. 10 cm^{-2} et un maximum hivernal de 1.23 mg. 10 cm^{-2}, la valeur estivale étant statistiquement plus faible du fait de l'état anoxique caractérisant les sédiments en certains points (Fig. 3).

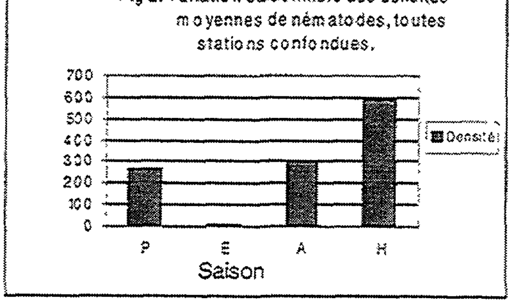


Fig 2: Variation saisonnière des densités moyennes de nématodes, toutes stations confondues.

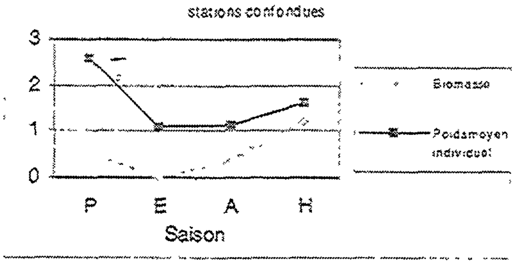


Fig 3: Variation saisonnière de la biomasse totale et du poids individuel moyen des nématodes, toutes stations confondues

Fig 4· Variation spatiale des densités moyennes de nematodes pour l'année 1996.

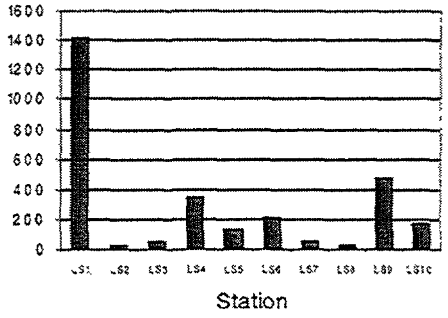
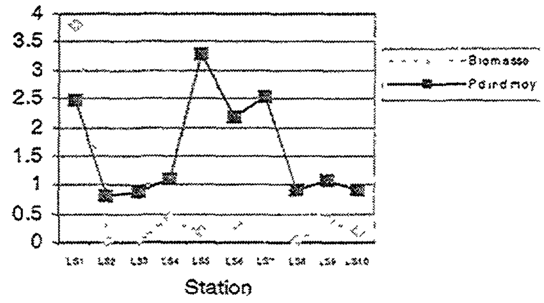


Fig 5: Variation spatiale des moyennes de la biomasse totale et du poids individuel moyen des nématodes pour l'année 1996.



Le poids moyen individuel qui est un paramètre dépendant davantage de la composition spécifique que de l'effectif communautaire, varie lui aussi saisonnièrement mais de façon moins tranchée. Ainsi, sa valeur qui atteint 2.58 µg au printemps est significativement différente du minimum de 1.1 µg observé en été (Fig. 3).

Sur le plan spatial la station du canal de Radès, la plus proche de la mer et la moins polluée organiquement, apparaît, toutes saisons confondues, la plus peuplée avec un effectif moyen de 1420 individus. 10 cm^{-2}, lequel est significativement plus élevé que les moyennes de 29 et 33 individus. 10 cm^{-2} relevés respectivement aux stations plus confinées LS2 et LS8 (Fig. 4). Les densités étant significativement corrélées à la biomasse totale, la communauté à la station du canal de Radès présente la plus forte biomasse moyenne (3.796 mg. 10 cm-2) (Fig. 5), ses valeurs saisonnières étant toujours plus élevées qu'ailleurs, sauf en été. La moyenne stationnelle du poids moyen individuel, très fluctuante oscille entre 0.82 µg (station LS 2) et 3.28 µg (station LS 5), les valeurs de la biomasse moyenne d'un nématode présent à la station LS1 étant significativement ou très significativement plus élevées que celles observées aux autres stations confinées LS8, LS9 et LS10 (Fig. 5).

A l'échelle spatio-temporelle, les densités de nématodes, fluctuent entre un pic saisonnier maximal de 3577 individus. 10 cm^{-2} au niveau de la LS1 et un minimum de 10 individus. 10 cm^{-2} aux stations LS2 et LS7. Les conditions extrêmes qui sévissent en été sont responsables de la chute de l'effectif maximal saisonnier qui n'est plus égal qu'à 34 individus. 10 cm^{-2} et la disparition des nématodes aux stations les plus confinées LS3 et LS8. Les biomasses qui sont recensées à la station LS2 durant les saisons printanière et hivernale sont tout comme les effectifs particulièrement faibles et ne dépassent pas 0.0072 mg. 10 cm^{-2}.

Tous ces résultats confirment que les communautés de nématodes sont plus ou moins quantitativement affectées par la pollution organique qui caractérise le plan d'eau, les conditions ambiantes apparaissant plus rigoureuses en été qu'au printemps, notamment au niveau des stations occidentales, les plus éloignées de la mer.

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MODELLING OF ^{137}Cs CONCENTRATION CHANGE IN ORGANISMS OF THE JAPANESE COASTAL FOOD CHAINS

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In order to predict ^{137}Cs concentrations in marine organisms of Japanese coastal food chains, a basic compartment model being composed of nuclide transfer both from seawater and food chain was investigated. Food chain structure of typical Japanese coastal water is established to include detritus food chain, benthic food chain and planktonic food chain. The relation of uptake and excretion flux of ^{137}Cs in organism can be expressed as follows [1-4].

$$\frac{dB_n(t)}{dt} = k_{0n}\, S(t) + d_n D(t) - k_{n0}\, B_n(t)$$

where $B_n(t)$ represent ^{137}Cs concentration in organism of trophic level n, S(t) is the ^{137}Cs concentration in seawater, D(t) is the ^{137}Cs concentration in food organism or matter, t is the time (day), k_{0n} is the uptake ratio constant of organism, and k_{n0} is the excretion rate constant of organism. The d_{mn} is the uptake rate constant from food being derived by $d_n = \theta_n r_n$, where θ_n is the transfer rate of ^{137}Cs in digestive system in predator, r_n is daily ingestion rate of food by predator. Data of the transfer coefficients of ^{137}Cs for Japanese organisms exists as a result of many tracer experiment studies, and derived geometric mean of the reported coefficients were used for calculation.

TABLE I. OBSERVED VALUES OF CF AND DERIVED EQUILIBRATED VALUES IN MODEL.

	Observed CF		*Derived equilibrated Value (CF)*
Organism	^{137}Cs	Stable Cs	
Phytoplankton	-	-	22
Zooplankton	11	1-130	25
Algae	7-49	16-67	20
Plankton feeder	5-28	3-56	20
Detritus feeder	4-28	3-56	38

The equilibrated values of (^{137}Cs level in organism)/(^{137}Cs level in seawater) derived from calculation agreed with the observed data, indicating validity of modeling conditions (Table I). The result of simulation by this food chain model indicated the following conclusions.

1) "Ecological half-life" of ^{137}Cs in organisms of food chain were generally longer than the reported biological half-life derived from tracer experiments, indicating that there is a time lag in ^{137}Cs transfer through food chain. The result suggested that delay of the transfer is up to 20 - 30 % in organisms of lower trophic level and 60 - 90 % in organisms of higher trophic level.

2)The modelling makes it possible to predict the elevation of ^{137}Cs concentration in organisms being respond to the temporal introduction of ^{137}Cs into environmental seawater. The simulation showed, however, the ^{137}Cs concentration peak in organisms of food chain appeares 20 - 100 days later, and the concentration ratio (^{137}Cs in organism / ^{137}Cs in seawater) reaches only 3 - 4, in case of temporal ^{137}Cs introduction (3 days) to seawater. This result indicates insignificant contribution of short term ^{137}Cs introduction to organisms of coastal food chains.

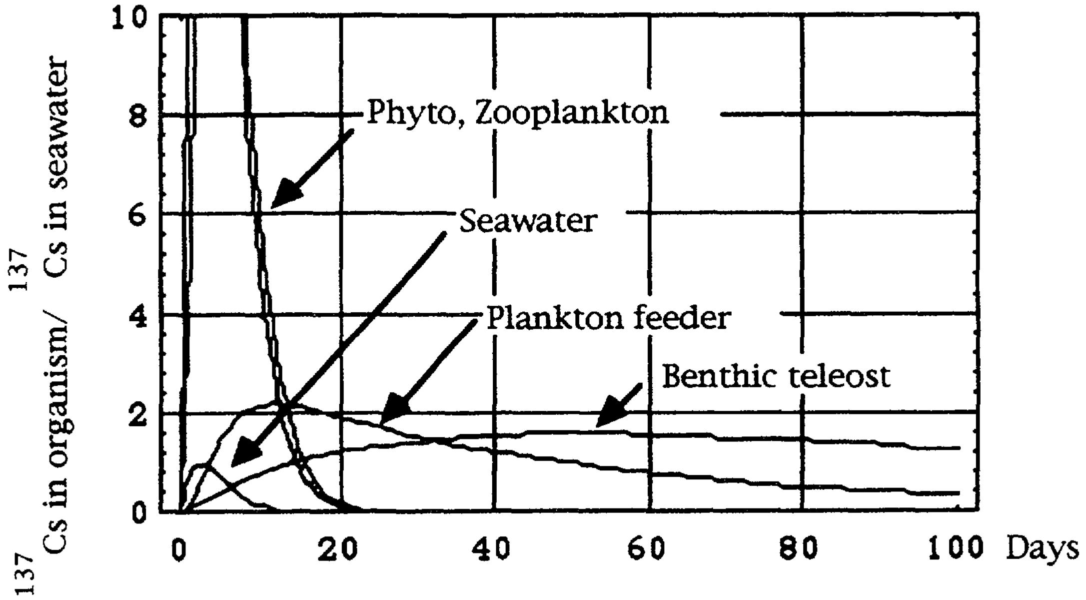

FIG. 1. Simulation of temporal elevation of ^{137}Cs concentration in organisms of food chain being respond to ^{137}Cs introduction to seawater.

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THE EFFECTS OF S-TRIAZINES ON SELECTED MARINE MACROALGAE

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Although s-triazines have been used as herbicides for many years, their use and that of other herbicides and fungicides, in antifouling compounds is only fairly recent. Very little published data exists concerning the toxicity of these compounds on non target marine algae and other organisms [1]. Research in UK suggests that in the years following the introduction of triazines as an active ingredient in antifouling paints, there has been an increase in the levels of triazines found in waters with high boating activity [2].The Hamble estuary, Hampshire UK has been identified as one such site. Investigations were conducted into the effects of s-triazines on selected marine macroalgae, local to that area.

Initially the investigation looked at the lethal effects of triazines on a range of macroalgae local to the hamble estuary. Pilot results on a limited number of common algae, indicated that only *Ceramium rubrum,* a red alga was susceptible to terbutryn at concentration less than 100 mg L^{-1} . With all other test algae showing no measurable effect at concentrations up to 100 mg L^{-1} . Other investigations indicated that sporelings were more susceptible than adult plants. Table 1 shows at LC_{50} (mg L^{-1}) values at four days for a wider range of algae. It can be seen that the most susceptible algae are *Fucus spiralis* and *C. rubrum,* mid to low shore species. The most resistant algae were the two large, mid shore species, *Ascophyllum nodosum* and *Himanthalia elongata.* The mid to upper shore species, *Ulva* spp and *Enteromorpha* sp, being moderately resistant to s-triazine.

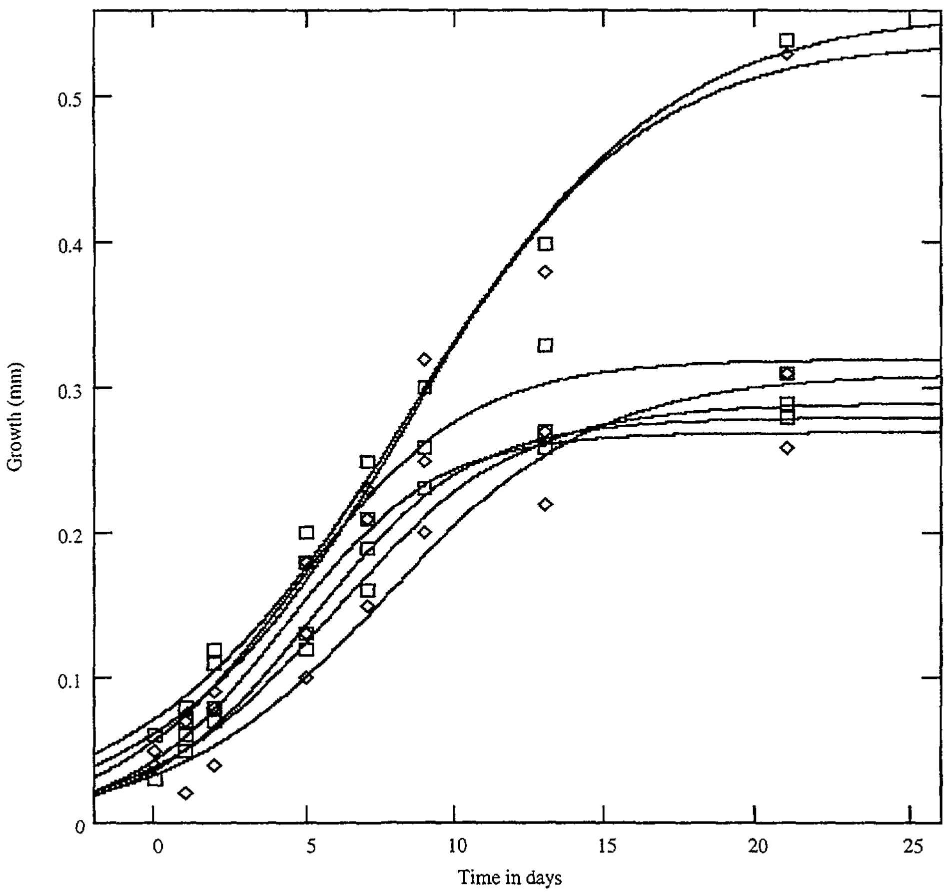
TABLE I. LC_{50} (mgL^{-1}) VALUES AT FOUR DAYS FOR S-TRIAZINES ON MARINE MACROALGAE

Alga	LC_{50} (mgL^{-1})
Ulva spp	25
Enteromorpha sp	20
Fucus spiralis	16
F.vesiculosus	25
Ascopyllum nodosum	66
Himanthalia elongata	100
Ceramium rubrum	17

Initially it appeared that the sensitiveness of the algae to s-triazine may be due to the position on the beach. However, consideration should also be given to the effect of the robust physical nature of the resistant species. All species seem to be tolerant to s-triazines than reported at other sites [3]. Algae, from a study near Plymouth, were taken from sites with very low levels of s-triazine. Algae from this study which were taken from s-triazine polluted sites. This leads to the suggestion that some algae may in fact may become resistant to pollution levels. Work is continuing in this area.

Growth experiments were conducted to investigate the sub lethal effects of s-triazines on marine algae. Apical sections of *F.vesiculosus* were grown in varying s-triazine concentrations over a range of temperatures for 21 days. Logistic curves were fitted to the algal growth data. Figure 1 show the effects of s-triazine on the growth at 22°C. It can be seen that concentrations of greater than significantly reduce the growth rate of *F.vesisculosus* after seven days exposure. At 15°C the growth of the alga is significantly reduced by concentrations of 10 mg L^{-1} but with the significance in growth reduction seen earlier at five days.

Fig 1 the effects of s-triazine on the growth of *F. vesiculosus* at 22 °C.



NB.Plots from top to bottom 0,1,10,25,50,75,&100 mg L^{-1}

Results from further experiments indicate that s-triazines affect the developmental growth of *F.vesiculosus* in the form apical division, the fertility of *F.vesiculosus*. Bifurcate division of the apical regions is significantly reduced in concentrations greater than 1 mg L^{-1} , and a significant reduction in the number of experimental plants becoming fertile at 10 mg L^{-1} . Preliminary experiments growing algae in varying levels of the toxin and salinity, indicate that salinity may play a significant role int he uptake of antifouling toxins by marine algae.

It can be seen that s-triazines, while be lethal to marine algae at levels higher than those reported to date, may well have a toxic effect at sublethal levels. S-triazines are photosynthetic inhibitors, a reduction in the photosynthetic effort will lead to a general reduction in metabolism. This is manifesting itself as a reduction in the growth, development and reproduction of these. The eventual environmental consequence will be a reduction in the algal biomass of coastal areas. While there is some indication the populations can adapt to these levels other indicators point to an increased stress by salinity variations leading to even more complicated picture of toxicity existing in estuaries, where boating activity is high..

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OXIDATIVE DRUG METABOLIZING ENZYMES IN NORTH SEA DAB (LIMANDA LIMANDA)(BIOLOGICAL EFFECTS OF POLLUTANTS)

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Increasing environmental pollution is regarded as an anthropogenic stress factor in general. As a consequence, this may have several detrimental impacts on organisms, including aquatic species.

The ability of organisms to tolerate stress from chemical pollutants depends on the availability of a variety of protection mechanisms. One important mechanism to protect cells from lipophilic xenobiotics is based on enzymes or enzyme systems converting the chemicals into more polar metabolites which can be excreted. Cytochrome P450 monooxigenases belong to this class of enzymes. They are also called mixed function oxigenases (MFOs). The MFO-system is a membrane-bound, non phosphorylating electron transport complex that is usually part of the endoplasmic reticulum of liver cells. The MFOs participate in a wide variety of reactions including desaturation and hydroxylation reactions, and they will metabolize both exogenous (e.g. xenobiotics, drugs, pesticides, hydrocarbons) and endogenous (e.g. steroids, fatty acids) substrates to polar water-soluble products. That means, that there is a huge family of monooxigenases, all acting on different substrates, preferentially. One of them can be measured using 7-ethoxyresorufin as an artificial substrate. Thus, the name of this enzyme activity is 7-ethoxyresorufin-O-deethylase (EROD).

The EROD-activity can be induced. In particular planar molecules, such as some polychlorinated biphenyl's (PCBs) and polycyclic aromatic hydrocarbons (PAHs) increase the enzyme activity. As a consequence, it is suggested that the activity of the MFO-system in organisms might be an indicator of the degree of some chemical contamination. Therefore, the measurement of EROD-activity is recommended to be done in the framework of several international campaigns dealing with Biological Effect Monitoring techniques.

The EROD-activity in the liver of dabs, caught in the North Sea at different seasons and at different sites has been studied by several groups. But comparing the different results, an inconsistent, non interpretable figure revealed. In this context the physiology of fishes may play an important role. Indeed, there were already significant hints that EROD activity per se exhibits a seasonal rhythm depending on spawning time, i.e. on temperature as well. These reflections ran into a model describing the temperature dependence of EROD activity (1).

The following prerequisites were made for the model:

1. The gonadal maturation of dab from different regions in the North Sea starts in September.
2. The duration of the gonadal maturation depends on a specific temperature amount expressed as month degrees (mo x C°), the mean watertemperature during the gonadal maturation multiplied by the time, i.e. the integral of the temperature.
3. The seasonal variation of EROD-activity in dab is coupled with the gonadal maturation and thus the time of EROD-peak varies regionally according to the shift in the spawning time, which is different in the whole North Sea due to the temperature regime in it.

In order to test this model, i.e. the natural annual fluctuation of the enzyme, we took a complete annual survey of EROD activity in 1995, 1996 and 1997 with the fishery research vessel „Walther Herwig III". The data obtained have been statistically evaluated (2). As a result, male and female dabs show a seasonal cycle of EROD activity. The maximum is higher and earlier (in year) in male than in female dabs. The strong effect on EROD of temperature points at an integration into physiological processes (spawning-cycle, hormone-status) of EROD. Now, a discrimination between natural and anthropogenic effects can be tackled with. If this comes true, EROD-activity could be a useful biomarker for the Biological Effect Monitoring.

In general, these considerations are valid also for other biomarkers, e.g. those to be induced in response to radiation. There is known a lot of radiation inducible genes playing a possible role in cellular protection against radiation. For instance Keyse (3) analyses the functions of radiation inducible genes in the context of their possible roles in cellular growth processes, like cellular oncogenes, tumor necrosis factor (TNF), interferon or some DNA-binding proteins. Rahmsdorf (4) demonstrates the activation of epidermal growth factors (EGF) by UV-radiation followed by the induction of signal transductions pathways. The German Federal Agency for Radiation Protection (BfS) lists in its latest annual report (5) some investigations into somatic and genetic effects of radiation. But, such signal transduction pathways may be physiologically steered, too. Difficulties arise from the discrimination between natural effects (e.g. temperature, hormones) and stress factors like radiation, especially low level radiation.
Thus, the modulation of the EROD-activity shown above may serve as an example of the problems with discriminating between natural and anthropogenic effects of stressors, in general. In summary, to evaluate effects of stress factors in a correct manner, it is necessary to have knowledge about natural fluctuations of the respective biomarkers. This should be discussed in more detail.

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XA9951954

UPTAKE AND METABOLISM OF ^{14}C-CHLORPYRIFOS BY MARINE BIVALVES

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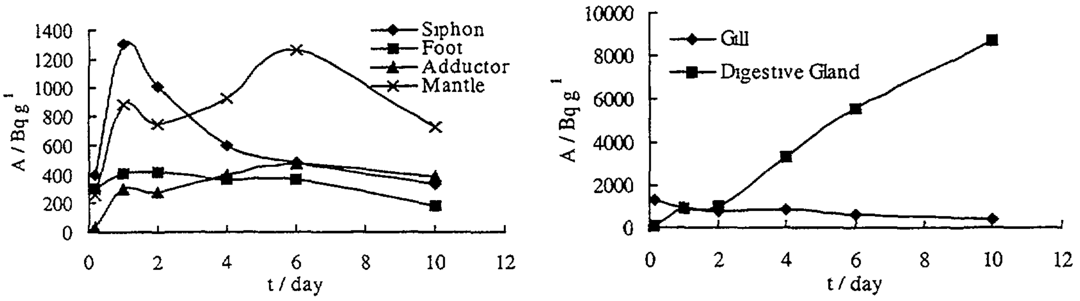
The uptake and metabolism of ^{14}C-chlorpyrifos by two marine bivalves, *Paphia undulata* and *Sinonovacula constricta,* were studied in a simulated ecosystem The experiments were carried out in two 30 L glass tanks containing each 20 L of filtered sea water, contaminated with ^{14}C-chlorpyrifos 1 85×10^{4}Bq L^{-1} (16 7 μg L^{-1}) at the beginning of the exposure period At different time intervals, three specimens of each species were sampled for analysis of the pesticide in the mollusc's tissues The ^{14}C-chlorpyrifos residues were extracted from the digestive gland of the molluscs and analyzed by co-chromatography with pesticide standards by TLC methods described before [1]

Fig 1 Uptake of ^{14}C-chlorpyrifos by organs of Paphia undulata



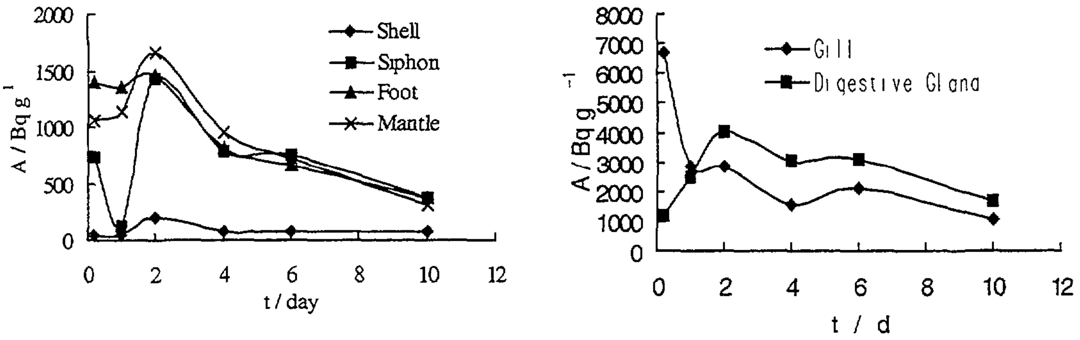


Fig 2 Uptake of ^{14}C-chlorpyrifos by organs of Sinonovacula constricta.

The results showed that the uptake kinetics of chlorpyrifos was different in the two species (Fig 1 and Fig 2) In *Paphia undulata*, the siphon reached the maximum uptake of the pesticide on the 1st day and declined afterwards, the maximum concentration in the gills was attained after only 4 hours exposure and remained nearly at the same level after that, and concentrations in the adductor muscle and foot were in near equilibrium from 1 day to 10 day It was notable that the digestive gland of *Paphia undulata* continuously accumulated the pesticide during the period of exposure The concentration of chlorpyrifos in this organ on the 10th day was about 10 fold higher than on the 1st day At the end of the experiment the concentrations of chlorpyrifos in the tissues were by descendant order digestive gland > mantle > gill > adductor > siphon > foot (Table 1)

The initial uptake of ^{14}C-chlorpyrifos by *Sinonovacula constricta* was higher than by *P undulata* but, unlike the later, the bivalve did not retain the pesticide for long time The peaks of

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*Present address. Amway (China) Co. Ltd, Guangzhou, P R. China maximum concentrations were observed in almost all the organs after 2 days of exposure, and declined significantly afterwards, approaching the same levels as in *P. undulata*. On the 10th day, the concentrations of chlorpyrifos in the tissues were by decreasing order: digestive gland > gill > siphon > foot > mantle > shell (Table I).

TABLE I. CONTENT OF CHLORPYRIFOS AND CONCENTRATION FACTORS IN THE BIVALVES

	Paphia undulata				*Sinonovacula constricta*			
Organs	1 day		10 day		1 day		10 day	
	A/Bq.g^{-1}	CF	A/Bq.g^{-1}	CF	A/Bq.g^{-1}	CF	A/Bq.g^{-1}	CF
Shell					152	12	263	43
Siphon	4808	390	1229	293	468	38	1371	453
Foot	1492	121	691	217	4987	404	1352	401
Adductor	1099	89	1443	283				
Mantle	3264	265	2698	766	4199	340	1166	433
Gill	3370	273	1474	376	10472	849	4000	1286
Digestive Gland	3418	277	32067	3380	9204	746	6118	1882

Analysis of the pesticide extracted from the digestive glands revealed that both bivalves lack the mechanisms to rapidly degrade chlorpyrifos. As shown in Table 2, the parent chlorpyrifos compound accounted for 92%~99.8% of the extractable ^{14}C-compounds in *Paphia undulata* and to 91.7%-99.6% in *Sinonovacula constricta*. The metabolites of chlorpyrifos, tri-chloro-pyridinol (TCP) and unidentified polar compound(s) remaining at the application point on the TLC plate, were present in negligible amounts. In previous experimental research with fresh water organisms, high TCP amounts were detected in the liver of a fish after 4 hours of exposure to chlorpyrifos dissolved in the water. However the amounts of TCP in the tissues of a freshwater clam (*Corbicula fluminea)* were also negligible[2], suggesting that, in general, molluscs have reduced capability to metabolise chlorpyrifos in comparison with fish. These results indicate that in the environment, molluscs may accumulate chlorpyrifos from water to very high concentrations with minor chemical degradation of the pesticide.

TABLE II. METABOLISM OF CHLORPYRIFOS BY THE BIVALVES

Animals	Residues	4 h	1 day	2 day	6 day	10 day
Paphia undulata	Chlorpyrifos (%)	95.21	96.26	97.59	99.78	92.68
	TCP (%)	1.38	0.44	0.08	0.07	2.32
	Unknown (%)	3.41	3.30	2.32	0.15	5.00
Sinonovacula constricta	Chlorpyrifos (%)	95.12	99.01	99.05	91.70	99.62
	TCP (%)	2.44	0.99	0	0.76	0.13
	Unknown (%)	2.44	0	0.95	7.54	0.25

Acknowledgements

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NUMERICAL MODELING OF DISPERSION OF POLLUTANT IN THE COASTAL ZONE OF THE WESTERN BLACK SEA

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During the last years in NIMH numerical models were used for forecasting the sea state in the Western Black Sea [2]. The recent developments in this field include a numerical model for computation the dispersion of pollutants in the coastal zone first of all the adaptation of the operational oil-spill model of Meteo-France for the hydrological conditions of the Black Sea [1] and under verification is numerical model for transportation of radionuclides as specific conservative tracers.

The oil spill response model of Meteo-France (MOTHY) is designed to simulate and forecast the transport of oil in three dimensions. The model is calibrated on several well-documented pollution incidents such as Torrey Canyon - 1967, Amoco Cadiz - 1978, Tanio - 1980, Gulf War - 1991, Aegean Sea - 1992 and the results are analyzed and described by *Daniel P.* [1]. The model consists of two models: a 2D non-linear model for the current dynamics in the upper mixed layer of the Black Sea and a model for the computation of the oil slick evolution. The equations of motion and continuity are used in spherical polar co-ordinate system of the "shallow water form" including advective terms and horizontal turbulence taking into account the seasonal dynamic of the upper mixed layer [4]. The equations are integrated forward in time on a Arakawa "C" - grid using a split-explicit finite difference scheme with surface wind and bottom stresses expressed in a quadratic relationship. The model uses very fine computational polar mesh of 2'*2' (approximately 2,528 * 3704 km with 42 000 grid points over the sea) that represents all significant features of the shelf topography and the coast line. The model was verified on storm surge data from the coastal tide-gauge observations along the Bulgarian shore during the recent years. The transport velocity fields are obtained in linear superposition of the climatological currents and the wind driven ones derived for every one studied period. The atmospheric forcing is provided by the winds and sea level pressure forecasts from the Meteo France model ARPEGE. This approach permits to obtain good approximation of the general circulation pattern for operational applications [1].

The oil slick is modelled as a distribution of independent droplets moved by current shear, turbulence and buoyancy. The current shear is calculated analytically for each one droplet with a bilinear eddy viscosity model according to the model of Poon and Madsen for predicting the near surface currents and the vertical current profile assuming the vertical eddy viscosity to increase linearly with the distance from both the surface and the bottom boundaries [1]. The turbulence is represented by a three-dimensional random walk technique. The buoyancy force depends on the density and the size of the oil droplets assuming that the lager and the more buoyant ones tend to remain in the surface layer, while the smaller droplets mix dow.

Results from the model verification presented here include the case of the storm winter period from 20.101994 to 10.11.1994. This period includes two storms and calm interval between them. Initial oil slick is assumed to be done in the location of the oil platform "Gloria" and on the tanker rout to the port of Burgas - Figs.1 and 2. The test runs for different possible sources of pollutants in the Western Black Sea indicated the great vulnerability of the Bulgarian coast. This is due to the specific features of the circulation over the Western shelf and the along shore currents in front of the Bulgarian shore that form several gyres on south of cape of Kaliakra. The basic Black Sea current structure move the pollutants along the shore and the local coastal gyres highly influenced by the local winds re-direct the transport in the direction to the shore. The model tests discovered the significant role of the seasonal currents and the accuracity of the surface wind forecasts for the precise computations of the oil drift in the Black Sea. At present the model is in operational use in NIMH as part of the marine forecasting system and it is also used for contingency planning and risk assessment.

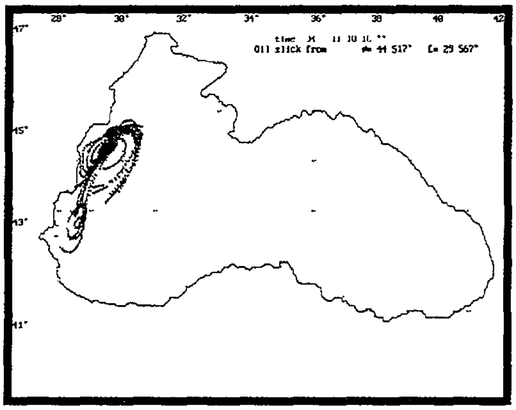

FIG. 1. Simulation of the oil slick from "Gloria" platform (44°31'N, 29°34'E) for the period from 20.10.1994 to 10.11.94.

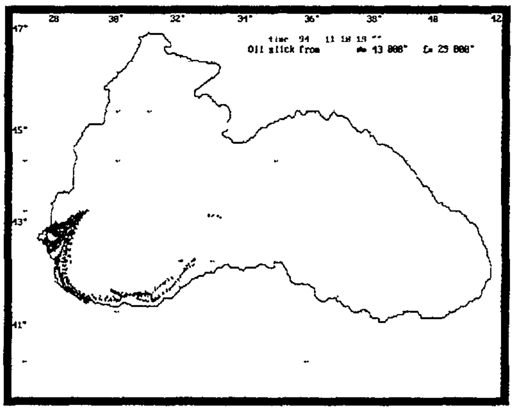

FIG. 2. Simulation of the oil slick from location over the tanker route (43°00'N, 29°00'E) for the period from 20.10.1994 to 10.11.94.

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TECHNOGENIC AND NATURAL RADIONUCLIDES IN BLACK SEA SEDIMENTS AND ALGAE

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Technogenic and natural emitters have been monitored since 1991 in marine samples from the Bulgarian Black Sea coast by low level gamma and alpha spectroscopy. The radionuclide content was determined in bottom sediment samples from 35 reference locations in the spring, summer and autumn during six consecutive years. Samples were collected and data obtained for the main Black Sea resorts and the main dwelling places along the Bulgarian Black Sea shore. The mean nuclide content depending on the year of sampling is shown in Fig. 1.

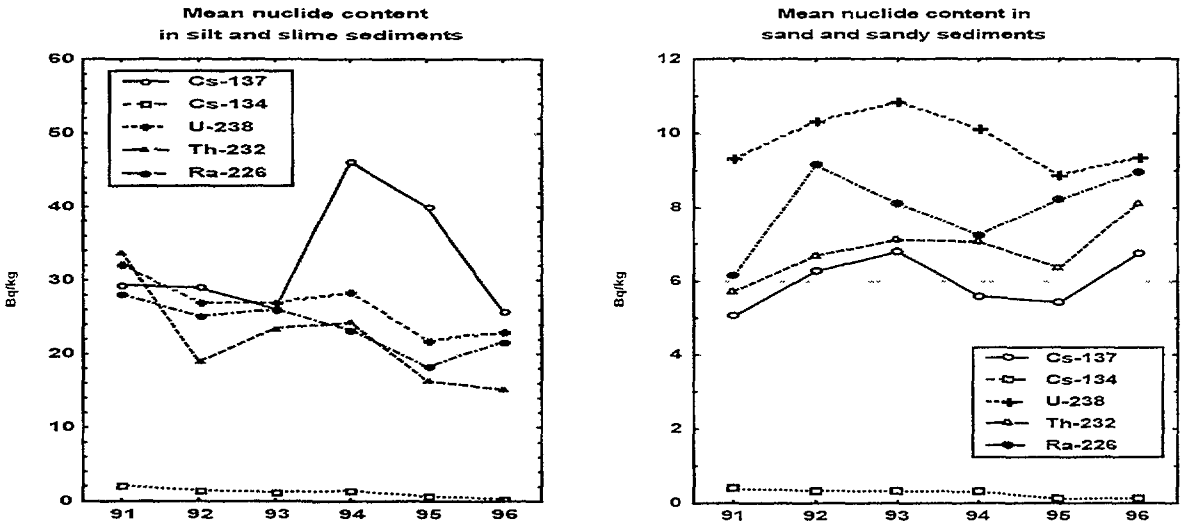

FIG. 1. Average nuclide content in bottom sediments.

The data show that nuclide content strongly depends on the sediment nature as the sandy sediments are within close range, while nuclides in slime and silt vary to a much greater extent. The highest measured cesium and natural nuclide content at the Bulgarian Black Sea coast is at the north locations with slime sediments - Kaliakra and Kavarna. This phenomenon can be attributed both to the sediments type and the shorter distance to Chernobyl.

(^{134}Cs/^{137}Cs) ratios were calculated for each location to determine the origin of the measured Cs in the Bulgarian Black Sea sediments samples. The calculations made show that 72 % from the whole measured ^{137}Cs in sea-bed sediments is from Chernobyl origin.

The highest values for natural nuclides content (Fig. 1) are in the slime sediments. The obtained results in different seasons for ^{238}U are (5 - 50) Bq/kg;^{232}Th - (4.0 - 35 Bq/kg), ^{226}Ra - (9 - 50 Bq/kg). The data show that there is a similarity between the accumulation of ^{238}U and ^{232}Th in the sediments. The measured U and Th values are within the range of the cited in the literature meaning that there is no serious contamination with U and Th at the Black sea coast.

We have investigated two different type of sediments by alpha spectrometry - slime (Kaliakra) and silt (Bjala) with the highest nuclide content. The content of different U, Th, Ra, Pb, Po and Pu isotopes for Black sea sediment samples are given on Fig. 2.

The values for Pu are close to the lower values of the cited in literature data which is quite clear as there are no plutonium discharge locations at the Bulgarian Black sea coast.

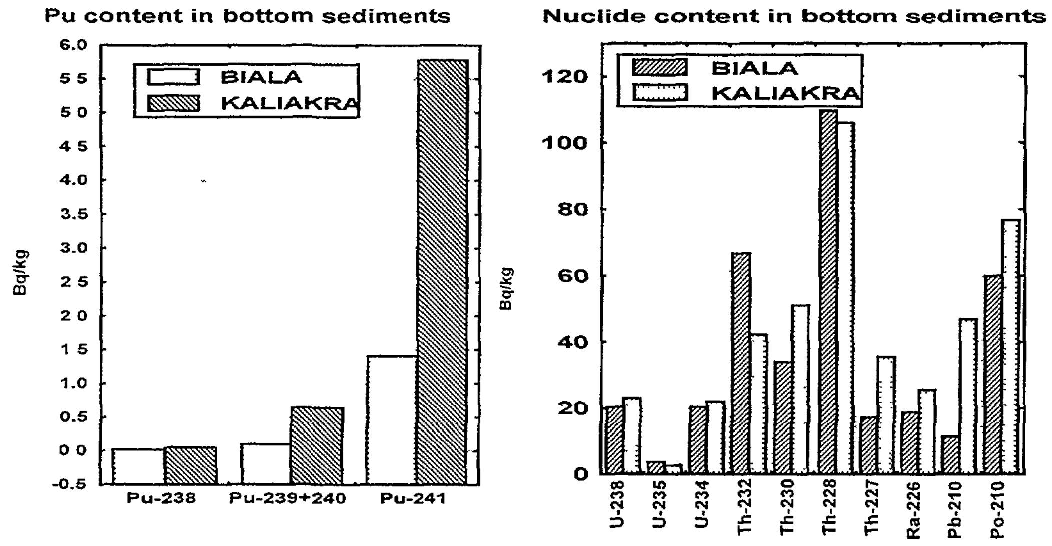

FIG. 2. Alpha nuclide content in Biala and Kaliakra sediments

Nuclide content was measured in nine different macrophytic algae species (Fig. 3) (five green: *Cladofora Laetevirens, Ulva rigida, Enteromorpha Intestinalis, Bryopsis Plumosa, Limnaea;* two brown: *Cystoseira Crinita* and *Cystoseira Barbata;* two red: *Ceramium rubrum* and *Corallina Mediterranium)* from five sampling locations for five consecutive years. The obtained range for ^{137}Cs in algae is 1.7 - 26 Bq/kg. The average values for the natural nuclides are: ^{238}U - 3 -44 Bq/kg; ^{232}Th (1.4 - 12) Bq/kg; ^{226}Ra (1- 52) Bq/kg.

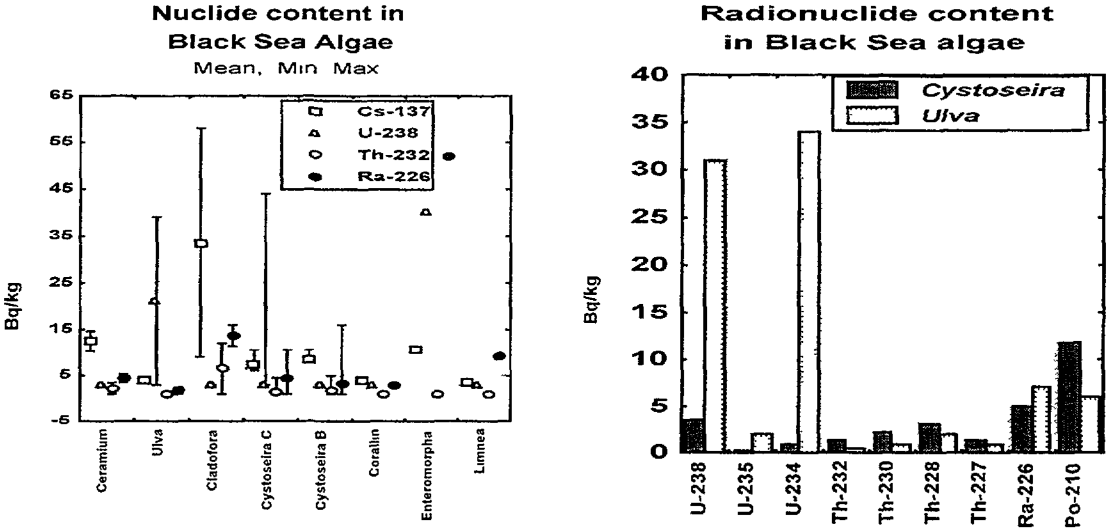

FIG. 3. Nuclide content in Black sea algae, measured by gamma and alpha spectroscopy.

The Cs content in the green species does not change greatly from site to site. Most of the natural radionuclide content is close to LLD while in *Bryopsis Plumosa* ^{226}Ra and ^{210}Pb and ^{232}Th concentrations are with two orders of magnitude higher then in the other algae species.

Natural nuclide concentrations were measured in two different types of algae are by alpha spectrometry (Fig. 3) and the data show that *Ulva* accumulates U more than *Cystoseira*, while the opposite is valid for Th. Ra is accumulated more efficiently than U by marine sediments and also by the brown algae. The Ulva, on the contrary, accumulates more U than Ra. The measured ^{210}Po content in Black sea algae is in the range cited in literature, the brown Cystoseira seems to accumulate ^{210}Po more than the green species.

This work establishes a data base for radioecological estimation of the Chernobyl impact on the sea bed sediments and the natural nuclide content along the Bulgarian Black Sea coast.

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MODELLING OF MIGRATION OF RADIONUCLIDES AND TRACE ELEMENTS BETWEEN THE COMPONENTS OF THE BLACK SEA ECOSYSTEMS

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As it is known, forecasting evaluation of the levels of hydrobionts and waters radioactive and chemical pollution, received with the help of mathematical models can be objective only when the structure and parametric base of the models depict with enough level of adequacy mechanisms of interaction under studies. Here an objective complexity of the model must correspond to the time and space scales, in which dynamic characteristics of the studied processes reveal themselves. This report considers peculiarities of the mathematical description of radionuclides migration between water environment and biotic and abiotic components of the Black Sea ecosystems at different periods of averaging, from the time scale of metabolic processes, taking place in hydrobionts, to the large-scale description of radionuclides migration in the Black Sea.

It is shown that kinetic peculiarities of radioisotope and mineral exchange in hydrobionts at the time scale of metabolic processes are described with sufficient level of adequacy by the equations, depicting zero and the first order of metabolic reactions. When radionuclide (tracing element) is absorbed directly from water medium and from food, kinetic of change in its countent in hydrobiont's exchange fund is described correspondingly by equations:

$$dC_g / dt = C_v K_c p - C_g(p + B'); \qquad (1)$$

$$dC_g / dt = R(C_f q - C_g q_f) - C_g p, \qquad (2)$$

where: C_v, C_g and C_f - concentration of radionuclide (or tracer element) in water, hydrobiont and its food correspondingly, K_c and p - stationary meaning of accumulation coefficient and index of the rate of radionuclide (element) exchange by hydrobiont, R and B' - ration and specific rate of hydrobionts specimens growth, q and q_f - level of food digestion and level of radionuclide uptake from the food, correspondingly, t - time.

According to the results of comparison of modelling data and experiments with radioactive marking it was stated that K_c value can depend on physical-chemical form of radionuclide, on the content of its isotope and non-isotope carriers in water environment, corresponding to Lengmur and Michaelis-Menten equations, and on size characteristics of hydrobiont specimen as well. It is shown, that equations of (1) type, written separately for reflection of the processes of physical and chemical sorption can be used for evaluation and forecasting the levels of ^{137}Cs concentrating by the Black Sea bottom sediments under changes of this radionuclide content in water environment.

Concentration and transfer of radionuclides by hydrobionts at the scale of the season and year ways of biogeochemical processes was considered on the examples of models creation according to the data of the Sevastopol bays radioecological monitoring and to the mathematical description of the flow of biosedimentational self-purification of the Black Sea photic layer, as a result of functioning of pelagic ecosystem in its Western halistatic zone.According to the data of mathematical description of the results of measurements of ^{90}Sr and ^{137}Cs concentration changes in the Sevastopol bays algae after Chernobul accident it was revealed, that the laws of changes in these radioisotopes content in algae were sufficiently described by (1) type equations. With this dynamics of the system «radionuclide in marine environment - hydrobiont» was determined only by the change in ^{90}Sr and ^{137}Cs contents in marine environment.

When studying water biosedimentativ self-purification, two-measure ecosystem model «phytoplankton - bacteria - zooplankton - dissolved organic matter - suspended organic matter in the photic layer of marine environment» was locked by balance in organic matter, biogenic element and water pollutant, which could attain the surface layer of the sea. Concentration of radionuclides (or tracing elements) by hydrobionts, and transfer of pollutions with trophic chains were descried by (1) and (2) types equations. Stability of calculative scheme for model realization was studied, its hydrological, hydrochemical and biotic parameters verification was fulfilled according to the results of the scientific cruises works in the region of the Black Sea western halistatic zone. The analysis of numerical solutions on the model has shown, that dynamics of the system as for pollutants was determined by the content concentrating function of hydrobionts relatively to pollutants and by correlation between an intensity of bioproductive and destructive processes in the photic layer ecosystem. It is established, that relatively to tracing elements it is possible to reach an extreme biosedimentational self-purification of waters, at which stationarity of the level of tracing element content in water environment can not be stated, as the flow of its getting into water environment can not be balanced by the flow of sedimentational elimination.

We studied peculiarities of modelling the large-scale processes of radionuclides migration on example of description of ^{137}Cs vertical migration in the upper layers of the Black Sea after Chernobyl accident. To reflect an action of the main averaged in the large-scale time and space imagination, abiotic and biotic factors on migration and the time of ^{137}Cs availability in the Black Sea the model was locked by water, salinity and radioisotope balance with consideration of radioactive decay. According of the model with hydrophysical parameters was carried out by water balance of the sea with consideration of river discharges, rains over the sea, evaporations and water exchange through the straits, and considering as well stationarity of the profile of vertical distribution of salinity. Verification of the model relatively to ^{137}Cs was carried out by comparison of the results of observations, begining from 1986, of averaged distribution of this radioisotope in the sea layers from the surface to 500 m depth. Radiocesium inflow with Dnieper and Danube and biosedimentational self-purification of water also were taken into account. Model studies have shown that the process of vertical water mixture is the main important factor of ^{137}Cs vertical migration in the Black Sea. It was revealed, that as a result of common effect of hydrophisical processes, transfer through the straits and sedimentational depositing in the bottom sediments, the time of ^{137}Cs availability in the Black Sea makes about 70-80 years, which is two times less than average time of existance of this isotope atoms.

Acknowledgements

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RADIOLOGICAL BACKGROUND OF THE GEORGIAN PART OF THE BLACK SEA

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Within the framework of the IAEA project RER/2/003 "Marine Environmental Assessment of the Black Sea Region" of which one of the aims is to investigate the effects of the Chernobyl accident on the aquatic environment of the Black Sea region [1], first investigations have been carried out for the Batumi region. It is planned to extend in the future the area of investigation to the whole of the Georgian area of the region.

Investigations of the technogenic changes of the radiation background of the Georgian part of the Black Sea and its coastal zone (Batumi region) were carried out during 1998. Samples of surface seawater, fish (Solea lascaris Pallas) silt, soil and vegetation (grass, moss, mushrooms, and lettuce) were collected on the coast of the Batumi region. The seawater samples were taken 2.5 nautical miles from the shore.

A new method of sorption of radionuclides (^{137}Cs, ^{90}Sr) from seawater samples was developed using natural zeolite (clinoptilolite) which is commonly found in Georgia [2]. This method allows to obtain a 20-40 g mass zeolite sample containing fully sorbed ^{137}Cs from 60-100 litres of water in a shorter time than by using usual methods. The better counting geometry (cf 50-100 ml water sample) increases counting efficiency by 10-15%.

Zeolite samples (5g dry mass) were heated with water (3 Bq/l of ^{137}Cs and salinity 15 g/l). Water passed simultaneously through four columns of dehydrated zeolite of equal length. The measurements confirmed the complete sorption of ^{137}Cs. Investigations of ^{90}Sr sorption are presently being carried out.

The ^{137}Cs extraction method using zeolite is ecologically preferable to traditional methods for the following reasons;

1. Simplicity of construction, cost effectiveness and easy to use.
2. Saving of time and energy.
3. Allows to control possible ^{137}Cs losses that the evaporation method cannot because of the volatility of ^{137}Cs.
4. Better counting geometry results.
5. Samples can be prepared in the field.
6. Easiness of storing and transporting the small amount of zeolite needed.
7. No pollutants are produced.

The obtained results for concentration of ^{137}Cs in seawater (Fig. 1) have shown levels between 20 and 30 Bq/l as could be expected. The biota samples (Fig. 2) have shown ^{137}Cs values in the range of 1-7 Bq/kg (a lower value for fish, a higher value for grass and lettuce), also in rough agreement with other observations in the region.

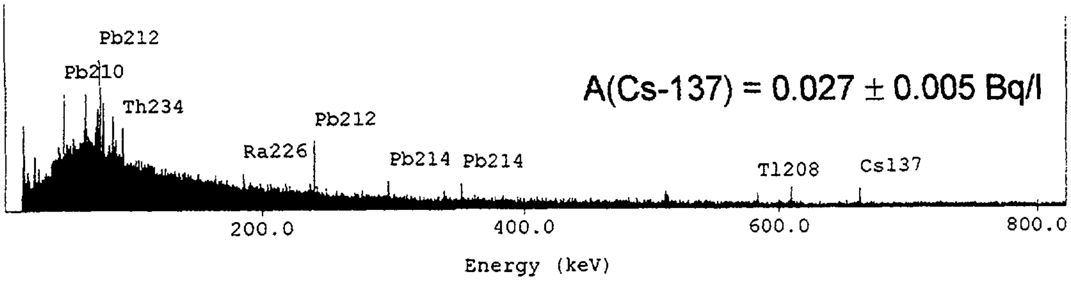

FIG. 1. Gamma-spectrum of surface seawater samples absorbed on zeolite.

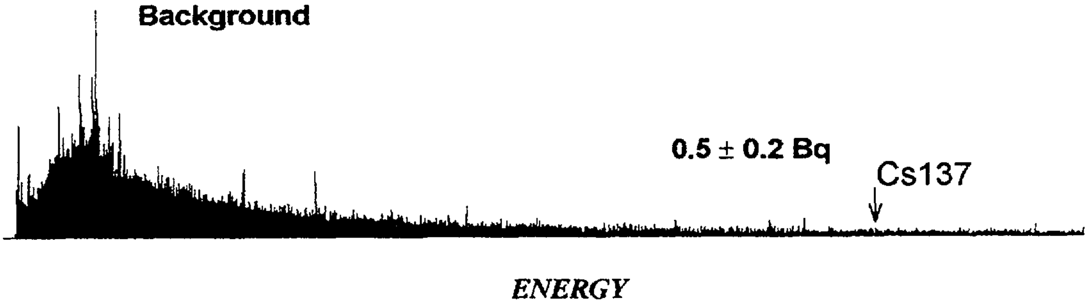

FIG. 2. Gamma-spectrum of biota samples (pkhali) from the Batumi region.

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DAMAGE TO THE TESTES OF A MARINE FISH, THE PLAICE (*PLEURONECTES PLATESSA*), INDUCED BY CHRONIC EXPOSURE TO LOW DOSE RATE RADIATION

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Although most authorised disposals of liquid radioactive waste are to the sea, effects of chronic radiation exposure on reproductive endpoints in a marine fish have not so far been investigated. For this reason we have carried out a series of experiments into effects of chronic radiaton exposure on plaice, a commercially important marine food species which spends much of its life in contact with sea bed sediments where exposure from radioactive contaminants have been shown to be highest.

In an initial experiment we found that exposure to continuous □-radiation at dose rates of 2.4 mGy h^{-1}, 1.3 mGy h^{-1} or 0 mGy h^{-1} (controls) for a period of about 5 months gave rise to dose-rate dependent reductions in testis weights which were significant even after the lowest dose rate of 1.3 mGy h^{-1}. In these fish, which were killed just prior to spawning, histometric analysis of sections showed that the decrease in testis weight was mainly due to significant reductions in sperm. However, it was not possible to ascertain whether direct effects on sperm or damage to earlier stages of spermatogenic development were responsible. The change did not appear to be due to effects on sex hormones as radioimmunoassay of blood samples for the main plaice sex hormones revealed no significant differences between irradiated and control fish.

Two further experiments have now been carried out in which male plaice were exposed to dose rates as low as 0.24mGy h^{-1}. In groups exposed to 1.02mGy h^{-1}, 0.51mGy h^{-1}, 0.24mGy h^{-1} or 0 mGy h^{-1} there was a dose-rate-dependent decrease in testis weight. The testis weights in all irradiated groups were significantly lower than in controls, Even in the lowest 0.24mGy h^{-1} dose rate group the reduction in testis weight relative to controls was approximately 50%. As in the initial experiment the fish were killed just prior to spawning and the reduction in testis weight was mainly due to reductions in amounts of sperm. In the other, similar experiment the dose rates were 0, 0.25, 0.5 and 1.1mGy h^{-1} and the plaice were killed after only 2.5 months at a time much earlier in the reproductive cycle when the main germinal tissue present was spermatagonia rather than sperm. There were no significant radiation effects on testis weight at this time but histometrical analysis showed that the proportion of testis occupied by spermatogonia was significantly lower than controls in all irradiated groups. This suggests that the radiation-induced reductions in testis weights observed after longer exposures to similar dose rates might have been due to damage to spermatagonia. However, further observations at regular intervals during exposure will be necessary to determine the primsry target for radiation damage with certainty. Examination of blood samples from these fish for genotoxic effects using counts of micronuclei and flow cytometric analysis of nuclear DNA content failed to show significant radiation effects.

This is the first time a marine fish has been examined in this way and the production of effects on reproductive tissue in plaice exposed to a dose rate of only 0.24mGy h^{-1} indicates the relatively high radiosensitivity of this tissue, higher than has been recorded for other fish and indicating a sensitivity similar to that in mammalian systems. The dose rate of 0.24mGy h^{-1} is about ten times greater than the maximum which was received by a few plaice in the NE Irish Sea off

Sellafield in the past [1]. However at the present time the maximum dose rate to the gonads of plaice living in this area is 0.6μGy h^{-1} [2] a factor of 400x lower.

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ASSESSMENT OF HEAVY METALS POLLUTION IN BOTTOM SEDIMENTS OF THE ARABIAN GULF AFTER THE GULF WAR OIL SPILL 1991

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The marine environment of the Arabian Gulf is becoming increasingly important in fulfilling social, economic, development and strategic objectives of the region. An estimated 6.3 million barrels of crude oil were discharged into the gulf between 19 and 28 January 1991. The Gulf war oil spill 1991 has necessitated major marine environmental studies to assess the extent of pollution on water, biota, and sediments. Sediments normally provides useful information in detecting pollution sources in the gulf system [1].

Eighty four surface bottom sediment samples were collected during LEG 1 of MT. Mitchell cruise during February 1992, covering the entire Gulf (Fig. 1). The major objective of this study was to carry out a sequential geochemical extraction scheme for the partitioning of Fe, Mn, Co, Cu, Zn, Ni, Cr and Pb in the bottom sediments of the Arabian Gulf to detect any potential pollution impact on the gulf sediments following the 1991 gulf war oil spill, and to differentiate between anthropogenic inputs and natural background of heavy metals.

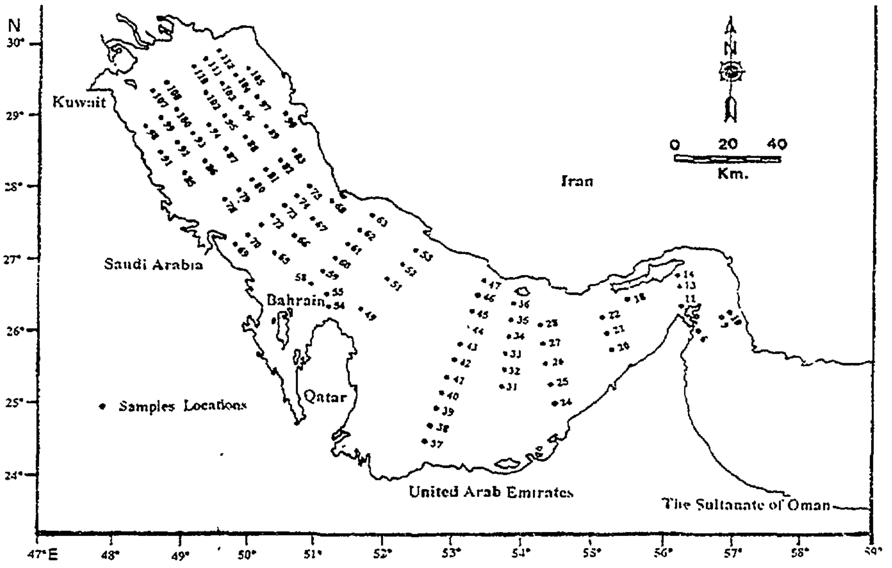

FIG. 1. Sampling stations.

Each individual sample was treated separately for determining the texture analysis, total organic carbon content, and total carbonate of the sediment samples. An analytical procedure in sequential extraction of heavy metals have been used to study the different extracted phases of trace metals, these phases are exchangeable phase (F1), bound to carbonate phase (F2), bound to Fe-Mn oxides phase (F3), bound to organic sulphide phase (F4) and residual phase (F5), [2].

Slightly elevated levels of studied heavy metals were observed in the fine sediments of the central area of the Gulf which characterized by high organic matter. Carbonates are regarded as trace metal diluters in the Gulf sediments. Low carbonates sediments in the NW region are characterized by elevated metal levels. Compared to values observed elsewhere in other areas of the world and previous levels in the Gulf, metal concentrations are at least an order of magnitude higher than heavily identified polluted areas in some other parts of the world.

With respect to the total metal concentrations in bottom sediment of the Arabian Gulf, the percentage levels of metals in exchangeable phase (F1) were recorded in little concentrations ranged between (0.1 %) as minimum for iron and (2 %) as maximum for Cu concentration in this fraction.

Regarding concentrations which were bound to carbonate phase (F2), Fe, Cr, are lower than their respective detection limit in other phasess. The levels of cobalt and zinc remain low (<5%) compared to the total metal concentrations, while it represent 8% for Cu, 11% for Ni and Mn and 22% for Pb.

The metals bound to Fe/Mn oxides phase (F3), with exceptional of Ni and Cu, are relatively high and represent a large fraction of the total non-residual metal concentrations where, Fe (37.9%), Co (33 %), Zn (53 %), Cr (30 %) and Pb (64 %). For metals bound to organic sulphides phase (F4), the levels of metal are once again lower than their respective detection to the total metal concentrations except for copper, zinc, cobalt and nickel which represent a significant proportional value to the total metal concentration. They account (25%) for Cu, (31%) for Zn, (32 %) for Co and (42 %) for Ni. The absolute concentrations for the others could follow the order Cr<Mn<Pb<Fe.

There are some metal concentrations found in the Residual phase (F5), higher than those observed in any of the preceding extractions. In the case of iron, copper and chromium, the residual fractions account for more than (50%) of total metal concentrations, in addition to manganese and cobalt, which they account (27%) and (29%) of total metal concentration in the residual phase, respectively.

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NEUTRON-INDUCED PROMPT GAMMA-RAY ANALYSIS OF GULF MARINE ENVIRONMENTAL SAMPLES

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Elemental analysis of toxic elements in major, minor, or even trace amounts is essential for solving several environmental pollution problems. Although many analytical methods can be used for environmental samples, there are only a few non-destructive analytical methods for light elements. A neutron-induced prompt gamma-ray analysis (PGA) is characterized by its capability for non-destructive multi-elemental analysis, for analyzing the light elements of H, B, N, S, P and Si which are difficult to analyze by other methods and for analyzing toxic elements of Cd and Hg. In addition, owing to the characteristics of non-destructive analytical ability and negligibly low residual radioactivity, the samples can be used by other analytical methods after analyzing by PGA, and consequently a large number of elements can be determined. Furthermore, isotopic analysis can be performed by PGA. Although PGA has the above mentioned advantages, previous PGA analyses carried out so far had the disadvantages of low analytical sensitivity and high detection limits due to the poor beam quality. The disadvantages have been substantially improved by using cold and thermal neutron guided beams as neutron sources for PGA. A highly sensitive and low gamma-ray background PGA system using cold and thermal guided neutron beams of 20 MW reactor JRR-3M has been constructed at the JAERI [1], and basic studies regarding elemental and isotopic analysis have been carried out [2, 3]. It was clarified that the analytical sensitivities and detection limits of the present PGA system are better than those of previous PGA systems due to the use of high quality, low energy neutron beams and a low background system. Using the PGA system, elemental determination by comparative standardization has been studied and accuracy, precision and detection limits for elements have been evaluated [4, 5]. The present PGA is being applied to the analysis of marine environment samples collected from the post-war Persian Gulf to study the oil pollution under collaboration between the JAERI and the IAEA-MEL.

Multi-element composition and isotopic characteristics of the oil and contaminated materials, and measurement of historical records of marine environmental condition using annual bands in coral samples have been investigated in the program. Elemental analyses have been carried out by the PGA together with INAA and ICP-MS to obtain accurate and precise elemental characteristics of oil, marine sediment and bivalves. Fifteen elements including light elements of H, B, N, Si and Ca which cannot be determined by INAA and ICP-MS, were determined by the PGA. Altogether 43 elements were determined. The PGA was applied to isotopic analysis of S in oils besides the elemental analysis of S. Capability of the PGA for accurate determination of isotopic ratio was tested by measuring the $^{32}S/^{34}S$ ratio in oil. The isotopic ratio of $^{32}S/^{34}S$ can be obtained with 2% precision by measuring 5420 and 4639 keV gamma-rays from ^{32}S and ^{34}S, respectively, in the pure S of natural isotopic composition. Differences in $^{32}S/^{34}S$ ratios among 5 different oil samples could not be detected. In the measurement of historical records with annual bands of coral, H, B, Na, Cl, Ca, Sr and Cd can be detected by the PGA in a coral sample (Porites lutia) "heads" collected in Qaru Island (Kuwait). From the distribution pattern of the trace elements in the coral sample, past marine environmental conditions can be evaluated. Analytical results of various oil samples are given in Table I.

TABLE I. ANALYTICAL RESULTS OF VARIOUS OILS

Element	At. No.	Analytical method	Crude oil Bahrain	Crude oil Egypt Red Sea	Crude oil Venezuela NBS SRM8505	Residual fuel oil NBS SRM1634b	Refined oil vacuum pump oil
Li	3	ICP	0.075	0.049	0.008	0.704	0.032
B	5	ICP		18.8	29.9		33.5
Mg	12	NAA	<460		<1700		
Al	13	NAA	9.37	16.5	20	50.2	23.1
S	16	PGA, NAA	23100	33000	25200	27800	9100
Ca	20	NAA	<190	<190	<140		<140
Sc	21	NAA	<0.0015	<0.0018	0.00665		<0.0012
Ti	22	NAA	<21	<48	<72		<7.3
V	23	NAA, ICP	20.9	128	375	55.6	<0.060
Cr	24	NAA, ICP	59.8	1.86	0.623		81.7
Mn	25	NAA, ICP	0.355	0.792	0.572	0.216	0.342
Fe	26	NAA, ICP	13.5	85.7	20.7	23.7	20.4
Co	27	NAA, ICP	0.091	0.299	0.597	0.166	0.236
Ni	28	ICP	2.74	8.07	6.96	18.2	1.78
Cu	29	ICP	0.305	0.566	0.47	0.756	1.15
Zn	30	NAA, CIP	18.3	4.32	3.42	10.4	1.99
Ga	31	ICP	0.116	0.145	0.162	0.133	0.211
As	33	NAA, ICP	0.127	0.017	0.078	0.123	0.153
Se	34	NAA, ICP	0.324	0.815	0.29	0.108	0.789
Br	35	NAA	<1.5	<4.9	<1.7		<3.9
Rb	37	ICP	0.912	0.846	0.891	0.961	1.43
Sr	38	NAA, ICP	0.552	0.536	0.932	0.429	0.752
Ag	47	NAA, ICP	0.006	1.44	0.014	0.033	0.024
Cd	48	ICP	0.018	0.137	0.032	0.079	0.128
In	49	ICP	0.025			0.135	0.202
Cs	55	NAA, ICP	0.127	0.003	0.134	0.017	0.104
Ba	56	ICP	0.001	0.361	0.04	1.25	0.493
La	57	NAA	<0.17	<0.22	<0.21		<0.19
Ce	58	NAA	<0.21	<0.22	<0.15		<0.17
Sm	62	NAA	<0.036	<0.048	<0.038		<0.032
Eu	63	NAA	<0.0062	<0.0090	<0.0053		<0.0040
Hf	72		<0.022	<0.025	<0.018		<0.016
Tl	81	ICP	0.102	0.004	0.081	0.226	0.044
Pb	82	ICP	0.125	0.19	0.357	2.46	0.39
Bi	83	ICP	0.067	0.015	0.054	0.184	0.141
Th	90	NAA, ICP	0.094	0.002	0.016	0.121	0.098
U	92	NAA, ICP	0.015	0.007	0.074	0.023	0.059

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IAEA-SM-354/38P
XA9951962

DETERMINATION OF ^{237}Np IN SEDIMENTS AND SEAWATER

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Compared to other transuranic elements such as Pu and Am present environmental levels of Np are very low. Neptunium nuclides are therefore of little radiological significance in the concentrations found in the environment. In the longer term, however, ^{237}Np will become one of the most important radionuclides remaining in high-level radioactive waste. We have further developed a new method for analysis of neptunium in large samples of soil, sediment and seawater. The samples are measured on alpha detectors and by ICPMS (Inductively coupled plasma mass spectrometry)

Pre-concentration of neptunium is carried out by scavenging with $Fe(OH)_2$ from 10 g sediment leaching solution or 100 litres seawater during the presence of SO_3^{2-} - Fe^{3+}. The sample is dissolved in HCl and $Fe(OH)_3$ is precipitated at pH = 9 with NH_3 (to remove the Ca^{2+},Mg^{2+}) and at 0.3 M NaOH (to remove the amphoteric elements). $Fe(OH)_2$ is precipitated again at pH=10 during the presence of $K_2S_2O_5$ and dissolved in HCl .The acid should be 8 –10 M HCl in 50 mL. The $NpCl_6^{2-}$ and $UO_2Cl_4^{2-}$ are extracted into 50 mL 10% TIOA/xylene and Pu^{3+} is left in the solution. The Np^{4+} is back-extracted with 2 M HCl and $UO_2Cl_4^{2-}$ remains in organic phase. The back-extraction solution is diluted to 150 mL with H_2O and 200 mg $K_2S_2O_5$ and 60 mg Fe^{3+} are added to the solution. The solution is basified with NaOH to pH = 10 to form $Fe(OH)_2$ which is centrifuged. The $Fe(OH)_2$ is dissolved in 1 mL 12 M HCl and diluted to 10 mL. Add 13 mL HNO_3 to the solution. Stir and stand for 10 min. The solution is passed through the column (15 × 1 cm, 100-200 mesh, Ag1-X_4). The $Np(NO_3)_6^{2-}$ is absorbed on the column . The uranium is eluted with 80 mL 8 M HNO_3 and the thorium eluted with 40 mL 12 M HCl. Neptunium is stripped with 6 M HCl + 2 g NH_2OHHCl + 1 g NH_4OH + 3 mg NaCl. Add 3 mL 14 M HNO_3 to the solution and the solution is evaporated to dryness and heated to volatise the NH_4NO_3. The sample is dissolved in 10 mL 0.5 M HNO_3 for ICPMS measurement or electrodeposited on the disc for α-spectroscopy measurement. The flow sheet is shown in Fig. 1.

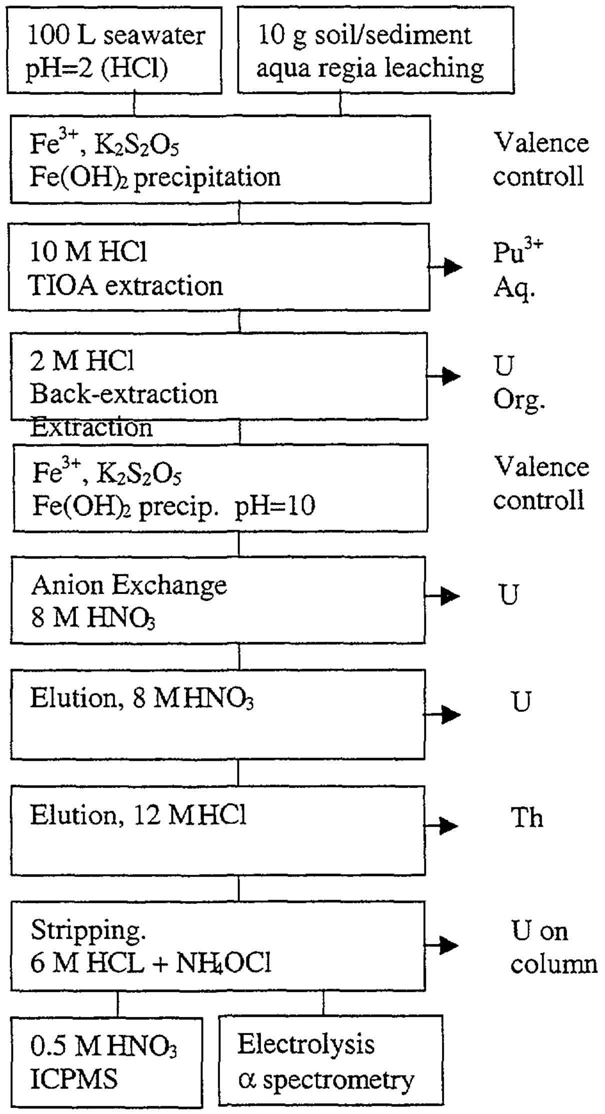

FIG. 1. Flow Sheet

The developed procedure introduces a new method for controlling the valence state at Np^{+4} by applying the redox system SO_3^{2-} / Fe^{3+} at low acidity. After adding 100 mg $K_2S_2O_5$ and 60 mg $FeCl_3$, the Np^{+4} is characterised by being extracted in the organic phase of 10 mL 0.5M TTA/xylene – 10 mL 2M HCl. Four repeated experiments gave a recovery of 98.6% ± 1.3% (SD) of the added ^{237}Np.

TABLE I. ^{237}Np RESULTS USING THE DESCRIBED PROCEDURE ON VARIOUS ENVIRONMENTAL MATERIALS INCLUDING TWO IAEA INTERCOMPARISON SAMPLES.

Reference	Matrix	Location	Amount	^{237}Np, Bq kg^{-1} or L^{-1} α-spectrometry	^{237}Np, Bq kg^{-1} or L^{-1} ICPMS
IAEA-300	Sediment	Baltic Sea	10 g	-	0.0012
IAEA-300	Sediment	Baltic Sea	10 g	-	0.0016
97160	Sediment	Urals	10 g	0.13	0.13
970014	Sediment	Urals	10 g	0.13	0.14
IAEA-381	Sea water	Irish Sea	0.5 L	0.0090	0.0085
IAEA-381	Sea water	Irish Sea	0.5 L	0.0092	0.0067

^{237}Np results obtained by applying the described procedure on various environmental materials including two IAEA intercomparison samples are given in Tab. 1. The Urals sediment sample '970014' was furthermore measured by TIMS in a US laboratory to 0.12 Bq kg^{-1} [1]. A set of 50 L seawater samples taken in the Danish waters at the entrance to the Baltic showed concentrations in the range 0.85 – 2.3 mBq m^{-3} measured by ICPMS. These levels are below detection limit by α-spectrometry, but well above detection limits for the used ICPMS system. The error in the tabulated data consists of the uncertainty from the average yield determination estimated to 10% and α-counting statistics (~10%) or ICPMS counting statistics (~1 - 10%); i.e. the combined error is estimated as ~10-14%.

In conclusion we can say:

- A new redox method applying SO_3^{2-}-Fe^{3+} has been developed. The method is well suited for preparing Np^{4+}.
- The redox system SO_3^{2-}-Fe^{3+} together with Fe^{3+}/Fe^{2+} act as a stabilising chemical reagent which keeps Np^{4+} and Pu^{3+} in their oxidation states during the separation of Np and Pu by TIOA/xylene extraction and in the anion exchange in 8-10 M HCl.
- The procedure for neptunium is simple and shows a good reproducibility of chemical yield: (92.6% ± 3.8)% (SD, n=8). Decontamination factors are $>5.2 \times 10^4$ for ^{234}U, $>1.6 \times 10^4$ for $^{239+240}$Pu, and $>4.4 \times 10^4$ for ^{232}Th.
- There is good agreement with results from a US lab using a different method on the same sample material [1] and data from ICPMS and α-spectrometry show comparable results.
- The procedure is an improvement compared to other methods, e.g. [2], and it furthermore improves laboratory safety by avoiding HF.

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IAEA-SM-354/39P

ENHANCEMENT OF ^{210}Po AND ^{210}Pb ARISING FROM PHOSPHATE INDUSTRY IN THE SYRIAN COAST

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Phosphate industry is considered to be one of the potential sources of natural radionuclide in Syria. Most of the phosphate processed ore is exported in large quantities via one of the Syrian main ports (Tartous) situated on the east part of the Mediterranean Sea (34° 54 N, 35° 52 E). Loading activities into ships have been carried out for more than 20 years. Dust carrying radioactivity is elevated and transported to the surroundings; most of the port area is affected. The impact of these loading activities on the marine environment has been evaluated. ^{210}Po and other natural radionuclides in seawater, sediment and marine organisms have been determined.

Sampling work was executed on the 22 of October 97 where surface sediments and sea water (50 l), fish and algae samples were collected from different sites inside and outside the port (Figure 1). The collected samples were measured by gamma spectrometry using hypurgermanium detectors to determine the gamma emitters while ^{210}Po and ^{210}Pb determinations were carried out by the standard methods used in EML, Monaco.

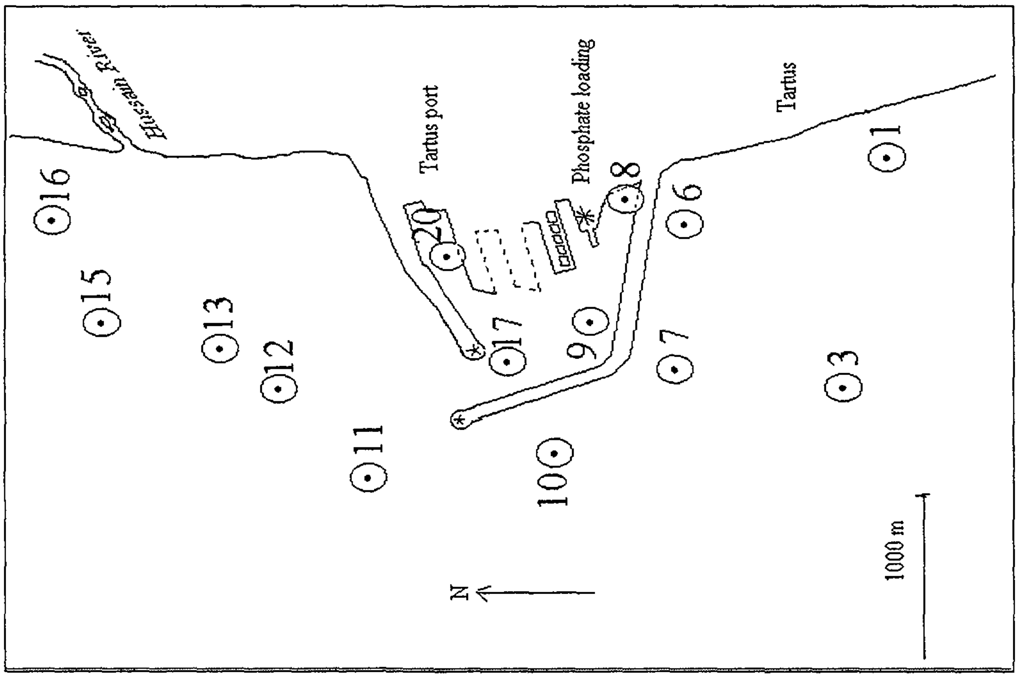

FIG 1. Sampling Sites (Mediterranean Sea)

Some of the results of ^{210}Po analysis of sediment, seawater, fish and algae are shown in Table I. The highest concentrations were found to be in those samples collected from inside the port area and this is due to the phosphate loading activities. The highest ^{210}Po concentration in sediment was 170 Bq/kg, which is much higher than those values reported for sediments, collected along the Syrian coast (1). However, these values are still much lower than those found in other areas in the world where similar discharges occurred (2,3).

Eleven species of fish were collected from the fresh catch sold in the local market and the location of the catch verified from the fishermen that being collected from outside the port. ^{210}Po was only determined in the edible parts and found to be in the range of 0.6 Bq/kg fresh to 27.48 Bq/kg fresh with a mean value of 6.3 Bq/kg fresh.

Other naturally occurring radionuclides were also determined in the collected sediment samples and relatively higher concentrations of ^{226}Ra (33.2 Bq/kg) and ^{224}Th(88Bq/kg) were found in those samples collected from inside the port area and especially near the loading platform.

The obtained data for ^{210}Po and other radionuclides shows a clear signal of technological enhancement of natural radionuclides inside Tartous Port. However, more samples will be collected next expedition and analyzed for ^{210}Po, ^{210}Pb and other radionuclides and the data will be presented.

TABLE I. ^{210}Po CONCENTRATIONS IN SEAWATER, FISH AND ALGAE SAMPLES COLLECTED ON 22/10/97

Site No.	Sediment(Bq/kg dry)	Seawater (mBq/l)	Fish (Bq/kg fresh)	Algae (Bq/kg fresh)
1	7.35 ± 0.7	7 ± 0.35	-	15.44 ± 1.2
3	21.92 ± 5.1	6 ± 0.32	-	-
6	29.86 ± 1.7	5 ± 0.23	-	-
7	39.11 ± 2.8	7 ± 0.36	-	-
8	100.27 ± 1.08	6 ± 0.33	-	-
9	150.88 ± 2.80	20 ± 0.58	-	-
10	30.82 ± 3.0	7 ±0.32	-	-
11	23.14 ± 0.7	-	-	-
12	69.0 ± 1.05	-	-	-
13	50.45 ± 3.4	19 ± 0.84	-	-
15	90.3 ± 4.9	7 ± 0.44	-	-
16	24.35 ± 0.3	8 ± 0.47	-	-
17	170 ±3.07	-	11.02 ± 0.65	7.54 ± 0.86
			23.09 ± 0.05	6.71 ± 0.46
			11.37 ± 0.5	7.28 ± 0.13
20	-	20 ± 0.65	-	-

Acknowledgment

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XA9951964

NATURAL AND MAN-MADE RADIONUCLIDE CONCENTRATIONS IN MARINE SEDIMENTS OF GOKOVA BAY, AEGEAN TURKISH COAST

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The Turkish coastal zone of the Aegean Sea has been heavily industrialized in the last 20 years, resulting in a considerable input of wastes to the coastal marine ecosystem. In the southern borderland and in particular in the shallow water Goköva bay, has been exposed to fly-ash materials from three major uraniferous coal power plants (CPP) since 1982. Although it is well known the signal enhancement caused by this kind of coal power plants, little information is available on the concentrations and distribution patterns of radionuclides, such as: U, Th, Ra, Rn and Po isotopes in the sediments.

The purpose of this research is to define a baseline study of selected radionuclides (natural and man made) on sediments collected along Gökova Bay. A total of six sediment cores (gravity corer) were collected, each sediment core was sliced in sections and ^{210}Po, ^{210}Pb, ^{226}Ra, ^{232}Th and ^{40}K and ^{137}Cs, ^{239,240}Pu, ^{238}Pu and ^{241}Am were determined for each layer of sediment.

The generation of electrical power using coal, oil or natural gas has the concomitant deleterious effect on the surrounding environment where these power plants are operating. The generation of 1GWe by a coal power plant (CPP) releases ^{220}Ra, ^{222}Rn, through fly-ash and gases at a rate of 10^9 to 10^{11} Bq y^{-1}; also generates 10^8 to 10^{10} Bq y^{-1} of ^{210}Pb, ^{210}Po, ^{226}Ra ^{228}Ra ^{232}Th ^{238}U (Baxter 1993). Despite the environmental regulations (trapping filters, etc) an important amount of the generated radionuclides are often found in airborne particles at each CPP. Turkey's need for electrical power relies on CPP. At Gökova Bay there are three major CPP, namely, Yatagan in operation since 1982, Yeniköy, since 1988 and Kemerköy since 1994. Yatagan has 3 units producing 210 Mw each, the other two plants in consideration have only 2 units of similar power. The ^{210}Pb activity on the coal used by these CPP range from 247-297 Bq kg^{-1} for Yatagan, 518-614 Bq kg^{-1} for Yeniköy and 730-863 for Kemerköy (Yener, 1995).

Six sediment cores were collected along Goköva Bay using a gravity corer with transparent PVC liners. The sediments were extruded and sliced every 10 cm intervals. Water content was determined by the difference between wet weight and freeze-dry weight. Salt correction was applied to all the weights measured. The following radionuclides were analyzed: ^{210}Po, ^{210}Pb, ^{226}Ra, ^{232}Th and ^{40}K and ^{137}Cs, ^{239,240}Pu, ^{238}Pu and ^{241}Am.

Overall, the concentration levels for man-made radionuclide on surface sediments were very low, only ^{239,240}Pu, ^{238}Pu and ^{241}Am were measured at the head of the Goköva Bay (G62) and at the middle of the bay (G39). *Perhaps the signal was underestimated (diluted) because of the coarse slicing of our* corers (0-10 cm intervals) and/or the hydrodynamic regime of the bay. G62 may represent a low energy environment with those stations located at the middle and mouth of this bay.

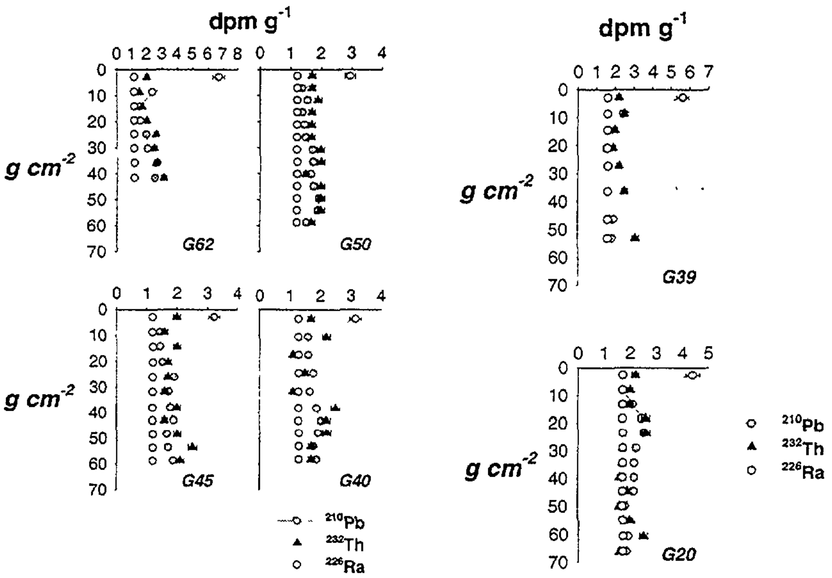

FIG. 1. Plots of total ^{210}Pb (orange circles), ^{232}Th (blue triangle) and ^{226}Ra (yellow circles)concentration profiles at each one of the stations (G62-G20) sampled. Also plotted are the counting errors.

All the other measurements were below our detection limits. ^{232}Th concentration were relatively high for these type of sediments (18.3 ± 2.8 - 51.7 ± 7.3 mBq g^{-1}), this may be related to local point sources.

With the exception of G39, in all the other stations excess ^{210}Pb did not reach equilibrium with ^{226}Ra at depth (> 60 cm) (Figure 1). Unfortunately ^{226}Ra was measured on few section for each core and their mean value used to calculated excess ^{210}Pb. Total ^{210}Pb inventories ranged from 1.7 to 2.6 ± Bq cm^{-2}; the highest value found in G20 and G62. The former is the close to Kemerköy CPP and G62 is located at the head of Bay away from the CPPs. Again, here the presence of the CPP may explain the activities found in G20 and the hydrodynamic regime at G62 may account for the values measured.

Although the number of stations as well as the resolution of our sampling (slicing) do not allows us to clearly define a distribution pattern in Gokövа Bay, it is possible to see that perhaps there is a link between the concentrations found in our samples with the locations of the stations relative to the 3 CPP in the area.

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XA9951965

HEAVY METAL POLLUTION IN THE SEDIMENTS FROM THE NORTHERN SHELF OF THE SEA OF MARMARA

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Heavy metal concentrations of the surficial sediments and total suspended solids (TSS) from the northern shelf of the Sea of Marmara (SM) were determined. The SM is a semi-closed basin connected to Black Sea and Aegean Sea through the two narrow straits of Istanbul and Çanakkale, respectively. The heavy metal contents of the sediments from the northern shelf donot show a large pollution. They represent intermediate values between the values of the adjacent seas' sediments, being higher than that of NE Aegean Sea and lower than that of Black Sea. Relatively high metal values were locally found in the Silivri Bay and off the Büyük Çekmece and Şarköy to Gelibolu coasts. Cu, Pb, Zn and Hg concentrations in TSS are higher than those of surface sediments, and more enriched in surface water TSS compared to near-bottom water TSS. However, Al, Fe and Mn concentrations follow almost an opposite trend. Considerably lower Al contents of the TSS compared to those of the surface sediments indicate a predominantly biogenic and municipal-waste origin for the TSS. Towards the west of the shelf, relatively high Fe, Mn and Zn contents of TSS in near-bottom waters and in surface sediments can be explained by effective flocculation of Mn as Mn-oxyhydroxides and scavenging of the other metals in a relatively oxygen-rich environment of the lower layer waters of Mediterranean Sea origin at the Marmara entrance of the Strait of Çanakkale.

A general increasing trend of metal contents in both the surface sediments and TSS in a west-east direction suggests that the studied shelf area is on the transport pathways of pollutants from the İstanbul metropolitan and the Black Sea. This is also in agreement with the seasonal changes in the circulation and hydrography of the SM; high metal concentrations in TSS are found during September and December when upper layer jet becomes weaker and tend to flow over the northern shelf.

TABLE I. METAL CONCENTRATIONS IN OFF-SHORE SHELF SEDIMENTS FROM THE NORTHERN SHELF OF THE SM AS COMPARED TO THE METAL ABUNDANCES IN EARTH'S COMPOSITION AND TO THOSE IN SEDIMENTS FROM ADJACENT AREAS AND SEAS

		Cu µg/g	Pb µg/g	Zn µg/g	Mn µg/g	Hg ng/g	Fe %	Al %
This Study	Mean	21	23	71	363	137	3.2	5.5
	St.D	7	6	17	137	63	0.8	1.4
	Range	7-44	11-35	38-131	101-616	48-361	1.7-4.5	2.4-7.6
Earth's comp. (Shale)	mean	50	20	90	850	300	4.7	9.2
Golden Horn Estuary (Istanbul)	range	333-3900	124-702	450-8750	333-565	NA	2.6-3.8	NA
İstanbul (Northern SM)	mean	32	32	89	253	251	2.9	2.44
Southern shelf of SM (Erdek Bay)	mean	28	40	125	384	500	3.0	7.2
Black Sea (southern shelf)	mean	49	34	87	570	NA	3.3	NA
North Aegean Sea (Saros Bay)	mean	19	22	73	451	52	2.8	5.7

TABLE II: THE MOBILITY PERCENTAGES OF METALS IN DIFFERENT REGIONS OF THE NORTHERN SHELF OF THE SM.

	Fe %	Mn %	Cu %	Pb %	Zn %
B. Çekmece (n=4)	0.65	28.0	6.9	26.8	10.7
Silivri K. (n=8)	0.99	23.5	9.6	32.8	9.9
Marmara E. (n=4)	0.8	25.2	7.5	22.0	7.6
Tekirdağ (n=4)	1.2	20.8	8.5	33.2	11.1
Şarköy-Mürefte (n=8)	1.9	28.0	10.2	27.0	8.2
Gelibolu-Şarköy (n=1)	2.3	25.0	7.4	32.8	8.1

TABLE III: MEAN METAL CONCENTRATIONS OF NEAR-SHORE SEDIMENTS DURING THE FOUR SAMPLING PERIODS. NA: NOT ANALYZED.

	Cu µg/g	Pb µg/g	Zn µg/g	Mn µg/g	Hg ng/g	Fe %	Al %
Dec. 95	29	24	75	468	NA	3.3	6.2
April 96	18	20	59	317	65	2.9	5.1
Sept. 96	19	17	63	334	169	3.3	4.2
Dec. 96	18	19	67	456	159	3.2	5.1
Off-shore shelf sediments	21	23	71	363	137	3.2	5.5

TABLE IV: MEAN AND RANGES OF METAL CONCENTRATIONS IN THE TSS SAMPLES COLLECTED DURING THE FOUR SAMPLING PERIODS.

	Cu µg/g		Pb µg/g		Zn µg/g		Hg µg/g		Fe (%)		Al (%)		Mn µg/g	
Dec 95	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
TSS	27	<17-157	181	<56-628	45	<5-292	3	0 6-7	0 1	0 01-0 4	0 5	<0 2-1 1	78	37-145
NS	29	17-47	24	12-39	75	23-107	NA	NA	3 3	1 4-5 1	6 2	4 2-7 8	468	281-650
Ap 96														
TSS	<17	<17-20	110	<56-595	56	10-89	0 6	0 1-1 7	0 2	0 04-1 1	0 4	<0 2-1 8	34	<14-85
NS	18	9-28	20	12-30	59	49-82	0 07	0 04-0 1	2 9	1 6-4 3	5 1	2 6-6 7	317	250-426
Sep 96														
TSS	41	<17-102	123	<56-1202	215	38-821	3	0 6-8	0 4	0 1-0 7	0 6	<0 2 -1 7	54	<14-126
NS	19	9-31	17	2-28	63	23-97	0 1	0 04-0 3	3 3	1-4 2	3 9	0 3-6 5	334	208-424
Dec 96														
TSS	18	<17-72	91	<56-434	89	<5-565	0 8	<0 2-2 4	0 1	0 02-0 4	0 2	<0 2-0 5	27	<14-87
NS	18	11-29	19	15-26	67	50-87	0 1	0 05-0 6	3 2	1 8-4 7	5 1	2 4-7 4	456	275-611

NS; “near-shore sedıments” from the same transects.

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XA9951966

BIOMAGNIFICATION AND BIOACCUMULATION OF MERCURY IN TWO FISH SPECIES FROM DIFFERENT TROPHIC LEVELS IN THE BAHIA DE CARTAGENA AND THE CIENAGA GRANDE DE SANTA MARTA, COLOMBIAN CARIBBEAN

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During the decade of the 70's a chlor-alkali plant dumped between 11 and 15 tons of mercury indiscriminately into the Bahia de Cartagena (BC), elevating the levels of this metal in the biotic and abiotic components of the ecosystem. Although two decades have passed since the plant was closed, the sediments of the bay seem to be an important source of mercury to the marine environment. The present work measured the contents of mercury in the sediment and determined the processes of bioaccumulation and biomagnification in two species of fishes of commercial importance: the parassi mullet (*Mugil incilis*) and the striped mojarra (*Eugerres plumieri*), a detritivore and an omnivore, respectively. Sampling was carried out during the months of March, May, August and November of 1996 covering two climatic seasons (dry and rainy). At each sampling individuals of both species were caught with fishig nets and surface (top 10 cm) sediments smaller than 63 µm were taken in six different stations distributed around all the bay. Simultaneously, the Ciénaga Grande de Santa Marta (CGSM), a coastal lagoon, was taken as an area of reference not affected directly by mercury contamination. Muscle tissue samples were digested in HNO_3/H_2SO_4 [1] and sediment samples in HNO_3/HCl [2], and mercury concentrations were measured with atomic absorption spectrophotometry (AAS) using the technique of cold vapor. The accuracy was periodically cheked by the use of reference samples.

The concentrations of mercury in the sediment, both absolute and normalized to the amount of organic matter, did not show significant differences ($P < 0.05$) through the year for each area, but significant differences were evident ($P < 0.01$) between areas where the concentrations of mercury in BC were three orders of magnitude higher than those found in the CGSM which were in turn within the natural limits of tropical habitats [3]; furthermore, the variability of mercury in the sediments of BC was far greater than in the CGSM due to the heterogeneous distribution of the sampling stations in relation to the distance of the stations to the current and past sources of contamination. This distribution was corroborated with an analysis of classification and ordination (Fig. 1)

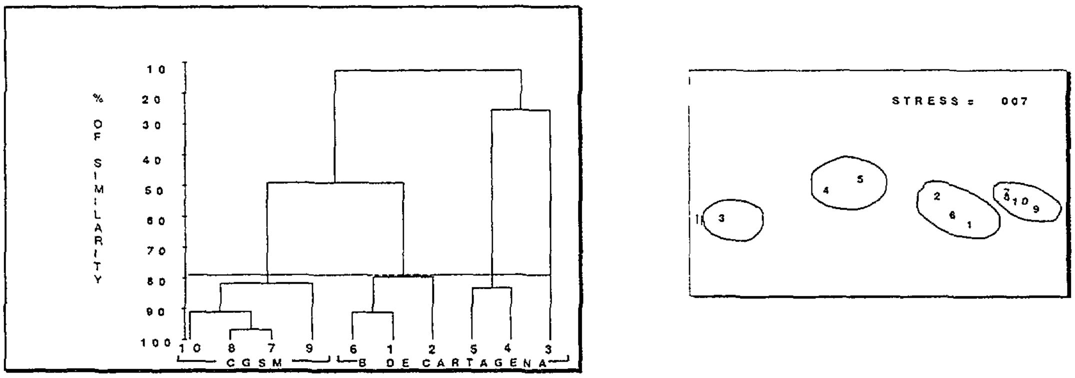

FIG 1. Ordination and classification analyses of the stations sampled for surface sediments normalized to the amount of organic matter Samples were taken in the Bahia de Cartagena (stations 1-6) and Cienaga Grande de Santa Marta (stations 7-10), from March to November, 1996

Mercury concentrations in mojarra were always higher that in mullet for both zones, but the differences were more significant in BC ($P < 0.01$) that in the CGSM ($P < 0.05$). The average concentration of mercury in muscle tissue for the bay was higher that in the CGSM, and it was in the order of 3 to 9.7 times greater for mullet than for mojarra, respectively. The mojarra in BC showed a relationship between mercury concentration and size and weight which was influenced by seasons.

The bioaccumulation of both species compared to the sediment was superior in the CGSM, an apparently contradictory result, which could be explained by a higher bioavailability of mercury in the area, and by the possibility that this species has not reached an equilibrium with the external environment [4]. For the mojarra the biomagnification factor (mojarra/mullet) was 4.1 times higher in BC than in the CGSM (Fig. 2).

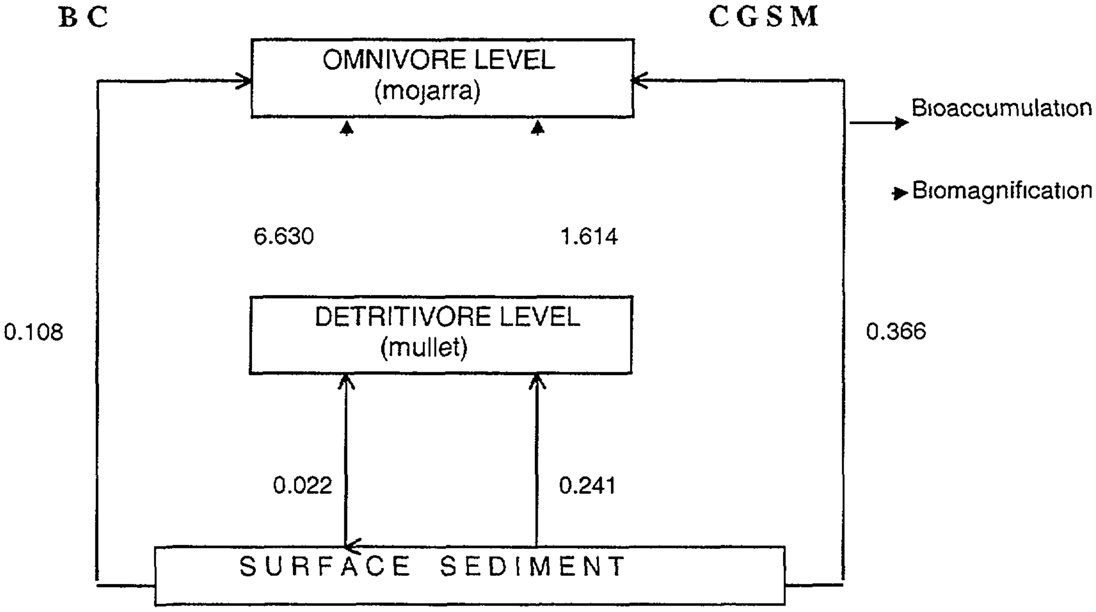

FIG 2. Average values for bioaccumulation and biomagnification in two fish species from two different trophic levels in the Bahia de Cartagena (BC) and the Cienaga Grande de Santa Marta (CGSM), from March to November, 1996.

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IAEA-SM-354/45P

STUDY OF BIOACCUMULATION OF MERCURY IN SHELLFISH (*Tapes decussatus*) FROM TUNISIAN COAST

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The mercury is found in the sea and lagoons at negligible concentrations which are affected directly with the tellurian supplies. The mercury accumulation could reach the toxic level and be noxious for both marine organisms and human being.

A national network for monitoring the shellfish production area has been created in 1995. The network aims to conserve marine ecosystem, living resources and human health.
The present work consists on determination of mercury concentration in the flesh of Veneridae (*Tapes decussatus*) locally called "clovisse or palourde." The total national production is estimated to about 1500 t/year and the 75 % is exported.

Six sampling areas were selected, two from the North and four from the South. For each area, the specimens collected during the summer of 1997 are grouped by sex and by category of size (Big>40mm, 35mm<Middle<39mm, 30mm<Small<35mm).

The sex is determined using a biopsy of the animal leg and the microscopic examination.

After the grinding and the lyophilization of flesh, the mercury concentration is measured by VARIAN AA 10 Atomic Absorption Spectrophotometer in cold vapor; [2]. With each batch of samples, a known certified standard (IAEA-MA-M-2/TM) was analyzed. The certified concentration of mercury of the standard material is 0,956±0,096 µg/g. We obtained a value of 0,910±0,075 µg/g. The results, expressed in µg of metal per g of dry tissue, were treated statistically using the following techniques:

a/Student t-test for the comparison of mean concentration
b/Honestly Significant Difference (HSD) of Tukey is used in the classification means mercury values by area.

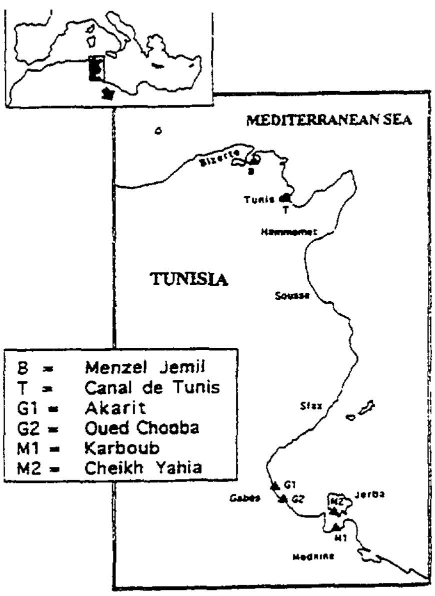

Fig 1. Sampling Areas. (Tapes decussatus)

The mean concentrations of mercury obtained by sex is plotted in figure 2 and that by size in Fig 3. The minimum and maximum concentration of recorded were 0,097 and 0,171 µg/g of dry weight. These values were below the limit level admitted by the World Health Organization (WHO). In fact, the cockles production areas are not yet mercury polluted. The cockles are filter-feeder which are exposed to local environmental mercury concentrations that are easily influenced by natural or anthropogenic sources [3].

The statistical analysis (Student test) showed no significant difference between males and females collected from the same area (North/North and South/South) and from two different areas (North/South).

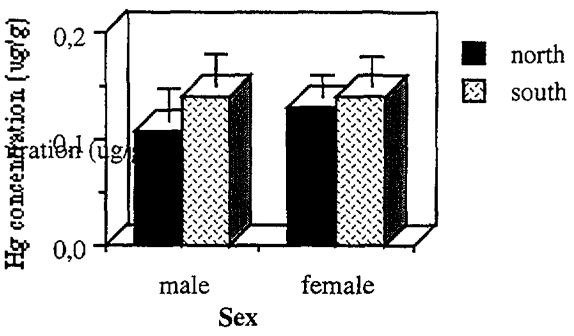

Fig. 2: Average concentration of mercury in Tapes decussatus determined by area and sex. Error bars denote standard deviation.

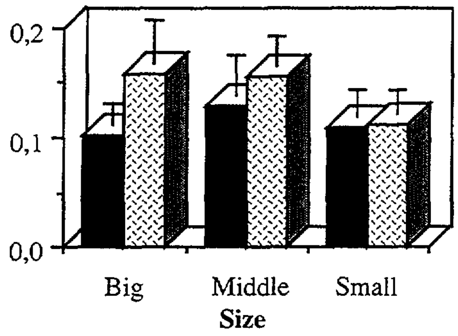

Fig. 3: Average concentration of mercury in Tapes decussatus determined by area and size. Error bars denote standard deviation.

However, a significant difference has been shown in south first between big cockles and small ones and then between middles and small ones. The comparison between areas (North/South) showed only a significant difference among the big cockles.

The classification of sampling areas depending on the determined mercury level is as follows : Bizerte (B)< Oued Chooba (G1) < Tunis (T) < Cheikh Yahia (G2) < Karboub (M1) < Akarit (M2). In fact the mercury concentrations in a sessile filter-feeder organism can change within very small distances [1].

The mercury levels in cockles has greatly contributed to a better understanding of the distribution of mercury concentrations.

The bioaccumulation mercury determined in cockles flesh collected from different locations aren't dangerous for human health.

On the basis of the findings and to minimize the monitoring network charges regarding its reliability, the following recommendations can be cited :

- The sex difference must not be considerate in the analysis.
- The mercury concentration levels recorded by category of size are clearly under the level admitted by WHO, so it will be judicious to treat all size mixed up together. The size will be considerate on the south area when we note that the mercury concentrations are increasing from year to year.

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IAEA-SM-354/47P

VERTICAL FLUXES OF PARTICULATE METALS IN A NORTHERN ADRIATIC COASTAL AREA

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Rivers are important carriers of suspended matter and dissolved elements from land to sea and their loads influence first of all the nearby coastal areas. The Northern Adriatic Sea is interested by the inputs of many rivers, among which the Po and Adige discharge in the basin the greater part of the total fresh water input.

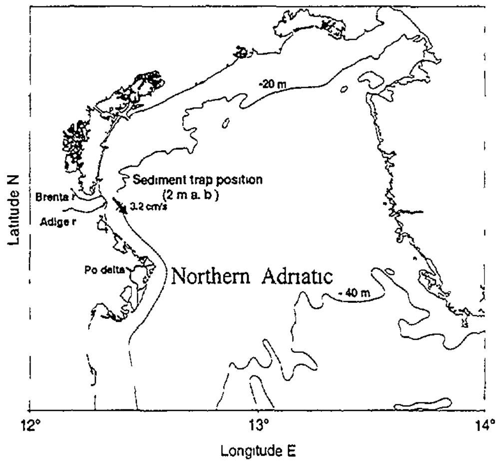

Fig 1. Study area and mean bottom current during the period April 1995-July 1996.

In order to determine the particulate fluxes and to characterise the suspended load of an area influenced by terrestrial inputs and interested by active sedimentation processes, suspended and sedimented matter samples were collected 2,3 miles SE from the Adige estuary, on the isobath of 20 m. The sediments of the area are characterised by clayey silts extending from NW to SE parallelly to the coastal line. From April 1995 to July 1996 samples of suspened and sedimented matter were collected, every 4 to 7 days, by a programmable sediment trap of 0,05 m^2 moored at 2 m above the bottom in a site influenced primarily by the Brenta and Adige rivers. The collections bottles were filled with 4% formaldehyde solution of in situ collected marine water, buffered at pH 8,2 with $Na_2B_4O_7$ and filterd on 0,4 Nucleopore filter.

Total and organic carbon were determined by CHN analyzer, before and after acidification with HCl respectively. Major elements (Al, Fe, Ca, Mg, Ti, Mn) and trace metals (Zn, Cr, V, Ni and Cu) were determined by inductively coupled plasma atomic emission spectrometry after HF/aqua regia microwave digestion. Currentmeter direction and intensity were registered 3 m above the bottom during the trap deployment. Wave heights, measured at the Acqua Alta platform 8 miles SE from Venice, were supplied by ISDGM-CNR (Venice). The suspended matter was collected by filtering large water volumes and metals were determined by ICP-MS (data supplied by IGM-CNR Bologna).

The gross sedimentation rate, averaged over the whole study period, was $27,5 \pm 48,1$ g m^{-2} d^{-1} and carbonates represent the major mineralogic fraction, constituting the 41,4 % of the sedimented matter.

The chemical composition of the sedimented matter is highly variable because of the influence of river discharge, primary production and resuspension processes in a high energy coastal environment. The concentrations of organic carbon and trace elements are lower than in the suspended matter but are higher than in the superficial sediments of this area, while Ca and Mg are more concentrated in the sediments.

Heavy metals are directly correlated with the river flow ($p<0,05$) and with Al and Fe ($p<0,001$); this indicates that terrestrial inputs influence the concentration of pollutants in the area and that heavy metals are preferentially associated with fine-grained particles.

Total flux, inorganic carbon and Ca are directly correlated with the significant wave height ($p<0,001$), while organic carbon is inversely correlated with it ($p<0,001$), showing that the main contribution to the gross flux is given by the resuspension of the bottom sediment, depleted in organic matter and rich in carbonates. For the same reason heavy metals (with the exception of Ni) and organic carbon show negative correlations with the gross sedimentation rate. A significative correlation was observed between wave height and the bottom currents ($r=0,49$, $p<0,01$) which arrive up to 46,2 cm s^{-1}. Resuspension events are generally caused by winds from NE or SE. The resuspension processes and the long shore bottom currents seem to play an important role in the southward transport of fine sediments.

Other important factors affecting particulate flux are the sedimentation of riverine fine-grained load and the settling of marine biogenic particles; the former is especially evident during late spring when there is a higher discharge of riverine water while the latter is more relevant during periods of low fresh water inputs and low sedimentation flux. The contribution of the resuspended flux to the gross sedimentation rate, estimated using the label approach [1] with Ca/Al ratio as indicator of the bottom sediment resuspension, is on average 43±23% while primary flux, determined using nitrogen as indicator, and advective flux, calculated as difference from the total, are on average 24±17% and 35±18%, respectively. A comparable contribution of primary flux to the gross sedimentation was found south of the Po delta by [2].

The seasonal variations of the gross sedimentation rates are primarily due to the meteorological conditions that cause, during winter a relevant resuspension, while the net flux (primary and advective) variations are mainly influenced by the discharges of the Adige and Brenta rivers and by the settling of marine organic particles. The possible contribution of atmospheric particulate deposition has not been estimated. The net settling fluxes range from 4.12 g m^{-2} d^{-1} in Spring 1996 to 24.14 g m^{-2} d^{-1} in Autumn 1995.

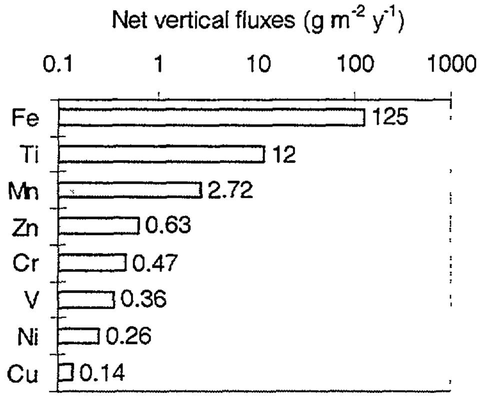

Fig. 2. Mean annual fluxes of heavy metals, corrected for resuspension effect.

The annual averages of the heavy metal fluxes, corrected for the resuspension, show higher values for iron, titanium and manganese, which are major constituents of the mineral matrix, and a relevant contribution of zinc and chromium with respect to vanadium, nickel and copper (fig. 2). A relevant part of the net vertical flux of Cu, Cr, Fe and Ti is of riverine origin, as also shown by the significant correlation of their concentrations with the Adige river flow, while Zn is strictly linked to the particulate organic carbon settling.

The particulate matter and, to a less extent, the sedimented matter results enriched in trace metals with respect to the surficial sediment; probably this is due to the higher amount of clays in the suspended matter. Resuspension processes play an important role, especially during the winter, in the remobilization and in the southward transport of sedimented matter and contribute on average for the 43% of the gross flux. A first estimate of the net vertical fluxes of trace metals in an area influenced by the discharge of two of the major North Adriatic rivers, besides the Po, has been attempted.

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XA9951969

CORAL REEFS AND EUTROPHICATION

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Coral reefs are found in oligotrophic waters, which are poor in nutrients such as nitrogen, phosphate, and possibly iron. In spite of this, coral reefs exhibit high gross primary productivity rates. They thrive in oligotrophic conditions because of the symbiotic relationship between corals and dinoflagellate algae (zooxanthellae) embedded in the coral tissue. In their mutualistic symbiosis, the zooxanthellae contribute their photosynthetic capability as the basis for the metabolic energy of the whole association, and eventually of a great part of the entire reef ecosystem.

Corals are adapted to nutrient-poor environments and can take up, retain, and recycle both dissolved inorganic and organic nutrients. Animal metabolism and zooplankton digestion by the host are the main source of nutrients for the zooxanthellae. Nutrients as dissolved inorganic compounds, are available also to the algae from the sea.

The population density of algae is controlled by nitrogen and carbon limitation. The coral host keeps the algal growth rate far from its maximum, as compared to growth rates in culture, and thereby ensures a supply of carbon translocated from the zooxanthellae. Additions of ammonium cause an increase in algal populations, and decreased translocation of carbon to the host [1,4,3]. There are three major ways by which increased nutrient supply may adversely affect corals and entire reefs [2].

A. Increase in phytoplankton populations in the waters surrounding the reef. Any increase in nutrient availability in oligotrophic waters invariably results in considerable increases in phytoplankton standing stocks, and thus an increase in chlorophyll *a* occurs, resulting in a decrease in the light availability to the underlying corals.

B. The increase in available essential nutrient increases the growth of seaweed. The onset of eutrophication removes the competitive advantage normally held by zooxanthellate coelenterates and opens the substrate to the invasion by the much faster growing seaweed, which now settle on any vacated substrate patch, dead coral, or even on wounds of live colonies. Overgrown by algae, eventually causes the death of corals a results of the combinations of conditions: 1)shading of the colonies severely curtailing photosynthesis of the zooxanthellae, 2) nighttime depletion of oxygen due to impeded circulation, 3) evolution of toxic hydrogen sulfide from the decaying algae and anoxic sediment. In the Gulf of Aqaba, upwelling of nutrients have resulted in overgrowth and smothering of the coral reef by the green seaweed *Enteromorpha* sp. and thus the death of the corals.

C. The increase in nutrients may affect the relationship between the zooxanthellae and the coral.

   I. The algae show significantly reduced photosynthetic rates due to carbon limitation in the super dense, multilayered algal population. The photosynthetic rates of nutrient enriched colonies of *Stylophora pistillata* increased compared to unenriched controls. However, there was a considerable decrease in photosynthesis per cell as zooxanthellae density increased. The coral growth rate was reduced.

   II. The increased algal population respires a larger share of the total, photosynthetically acquired carbon. The coral *Stylophora pistillata* from the Red Sea responded to enrichment with ammonium or ammonium + phosphate, mostly by increasing algal density. This was also found in colonies of *Pocillopora damicornis* from Hawaii (Table 1). An increase in algal density represents a breakdown of the balance between the host and the algae and results in decreased growth rate of the coral.

TABLE I: EFFECT AMMONIUM ENRICHMENT ON THE CORALS STYLOPHORA PISTILLATA AND POCILLOPORA DAMICORNIS[1,4].

Treatment	Areal chl a mg chl *a* cm^{-2}	Cellular chl *a* pg chl $cell^{-1}$	Area cell cell cm^{-2}
***S. pistillata* (Red Sea)**			
Control	1.82	3.00	6×10^5
N-enrichment	6.98	4.25	1.65×10^6
***P. damicornis* (Hawaii)**			
Control	1.40	7.714	1.96×10^5
N-enrichment	18.00	6.593	2.61×10^6

III. The zooxanthellae retain a much higher fraction of photosynthate, rather than translocating it to the animal. The zooxanthellae, while N-limited, have no use for most of the abundant photosynthate (C) they produce in excess of their own respiratory requirements, and the excess up to 95% is translocated to the host. Once supplied with additional nutrients, either as inorganic compounds such as ammonium and phosphate, or via zooplankton consumption by the host animal, the zooxanthellae retain most of their photosynthate, which they now utilize for synthesis of their own biomass.

The decrease in the contribution of each alga to the energy budget of the colony may have led to the observed decrease in the growth rate of the colony under nutrient enrichment conditions. Under increasing densities of algae resulting from nutrient enrichment, the algae may become CO_2-limited and may compete with the animal for carbon for calcification [1].

Coral reefs, on a local and regional scale, are exposed to many anthropogenic stresses, mainly eutrophication. Nutrient enrichment can introduce an imbalance in the exchange of nutrients between the zooxanthellae and the host coral. Reduces light penetration to the reef due to enhanced nutrient supply stimulates phytoplankton growth, and the most harmful of all, may bring about proliferation of seaweed. The latter rapidly outgrow, smother and eventually replace, the slow-growing coral reef, adapted to cope with the low nutrient concentrations, typical to tropical seas

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XA9951970

IAEA-SM-354/50P

EFFECTS OF HEAVY METALS ON THE BIOLUMINESCENCE OF THE OPHIUROID *AMPHIPHOLIS SQUAMATA* : A FIELD STUDY

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Amphipholis squamata is a cosmopolitan ophiuroid found in numerous marine habitats. The species is luminescent and the luminescence is under nervous control [1]. Reactives of the luminescence are not known, the only information gathered on chemistry of the luminous reaction being that it depends on calcium [2,3]. Expression of the luminescence is influenced by environmental physico-chemical parameters [4], among which also heavy metals. The latter contaminants may interfer either through direct effect on the luminescence chemistry or through alteration of the light production nervous control. Indeed, laboratory exposures to high concentration of Cd^{++} (5 to 10 mM) were shown to suppress the luminescence [2] and, in another ophiuroid species, to block electrical conductivity of the nervous system [5].

The aim of the present study was to investigate effects of heavy metals on the bioluminescence of *A. squamata* in the field. Therefore, ophiuroid populations were investigated along a pollution gradient in the Bay of Portman (Spain, Mediterranean) where 35 years of intensive mining activities resulted in a dramatic contamination of the marine environment by heavy metals (Fe, Pb, Zn, Ag, Cd, Cu).

Ophiuroids of the same size class were collected at three locations along a transect parallel to the coast and corresponding to a well-marked concentration gradient increasing from Station 1 to Station 3 [6]. Luminous performance of individuals was measured using 200 mM KCl stimulation to maximize the luminous reaction (all the luminescence reactives are involved in the reaction). Two parameters were used to characterize the luminescence performance: the intensity parameter (LMax) which is the maximal luminescence intensity recorded (in Relative Light Units per second, RLU/s) and the kinetic parameter (TLMax) which is the time to reach the maximal light intensity (in second, s). The luminescence was shown to be intense and fast in individuals from Stations 1 and 2, but 5-fold weaker and 10-fold slower in those from Station 3 (the most contaminated one) (Fig. 1).

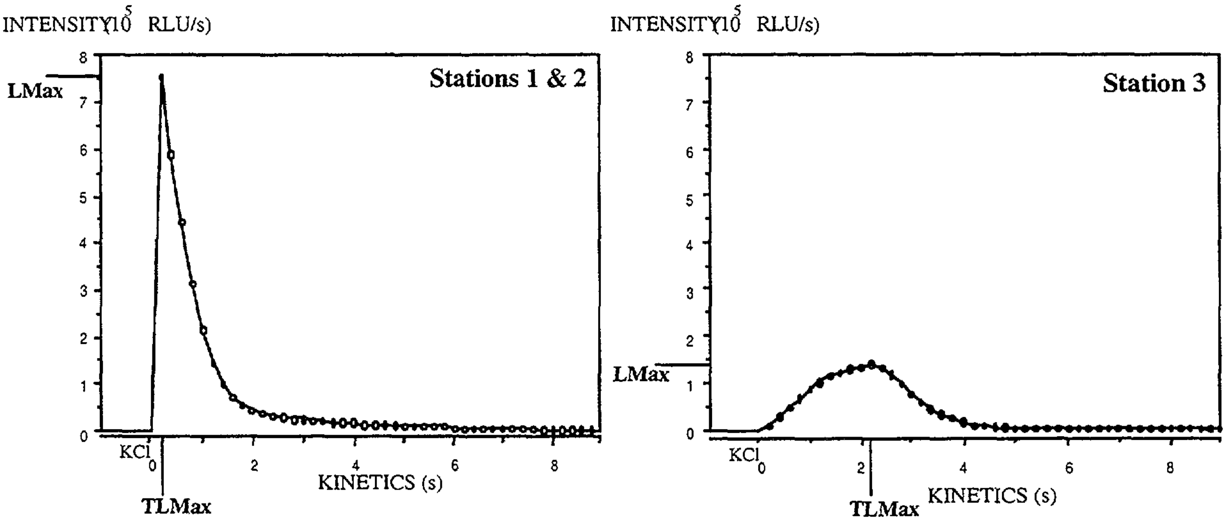

FIG 1: Typical luminescence records of Amphipholis squamata from Stations 1, 2 and 3

In another experiment, ophiuroids were transferred for three days from Station 1 to Station 3. These individuals showed no statistically significant moderation of luminescence following the transfer, although there was a clear trend towards a weaker and slower luminescence.

Results clearly demonstrate that heavy metal contamination declines the ophiuroid luminescent performance in the field. Since bioluminescence would be involved in intra- and inter-specific communications, the observed alterations in ophiuroid populations from highly contaminated environments could lead to a lower efficiency of their ecological adaptiveness.

The present investigation is a contribution to the Centre Interuniversitaire de Biologie Marine (CIBIM, Belgium).

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XA9951971

IAEA-SM-354/52P

MARINE RADIOACTIVITY STUDIES IN THE SUEZ CANAL: MODELLING HYDRODYNAMICS AND DISPERSION[1]

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This paper comprises the work carried out under the IAEA Technical Co-operation Project EGY/07/002 [1,2]. The main goal was to develop a modelling study on the dispersion of radioactive pollution in the Suez Canal. This effort is in connection with the increased public concern about radiation safety in transport through this important trade route. A model of the whole Suez Canal was necessary to follow the fate of radioactive wastes along this waterway. The model had to solve the hydrodynamics of the water governed mainly by tides, but also including atmospheric forcing and the drift currents produced by horizontal salinity gradients and by differences in MSL at the two entrances of the Canal. A modelling study, by using a 1D approach, has been carried out from available data. The basic hydrodynamic features of the Suez Canal resulted reasonably reproduced, despite some important lacks of information. The computed transit times vary enormously along the year, ranging from few days to several months, depending on the differences in MSL between the two entrances of the Canal.

In the second part of this work we took advantage of the two field tracing experiments carried out under the IAEA Project[i]. From their results, we developed a modelling study on the dispersion of radioactive pollution in the Taufiq-Gineva area. The experiments were accomplished by using rhodamine B as a tracer. During experiments, water levels, velocities, wind and other physical parameters were recorded to supply appropriate information for the modelling work. From this data set, we could reasonably describe the hydrodynamics of the studied area by means of a 1D-model. Then we are applying a 1D-Gaussian approach to predict the position and the spatial shape of the plume. Nevertheless, the required diffusion coefficient was strongly dependent on initial conditions. By means of a 2D-simplified model for dispersion, we are proving that a single formulation of diffusion, acting over a 2D structure with lateral velocity gradients, can satisfactorily explain the both two different observed dispersion patterns (see Fig. 1).

For the Bitter Lake area, where the previous method is useless, we are developing a 2D hydrodynamics and dispersion model to study the fate of any radioactive discharge. The bathymetry of the lakes is partially unknown and, consequently, the calibration of the hydrodynamic model from available data is only tentative. Nevertheless, and even with these limitations, the model is reproducing the basic observational hydrodynamic features. To solve 2D dispersion we are using the formulation of diffusion coefficients we previously studied from field tracing experiments in the southern Suez Canal area. In this way, we study different scenarios of discharges.

The main conclusion is that the dilution of concentrations will be a very slow process within this waterway where the tidal amplitudes of velocities are few cm/s in most of the Canal. This situation is specially critical in the Bitter Lake area. On the other hand, the seasonal changes in MSL at the Read Sea are greatly affecting the hydrodynamics of the whole system.

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[1] Work partially suopported by the IAEA-Technical-Cooperation Project EGY/07/002 (1994-96) and by contract I+D witth the Spanish ENRESA.

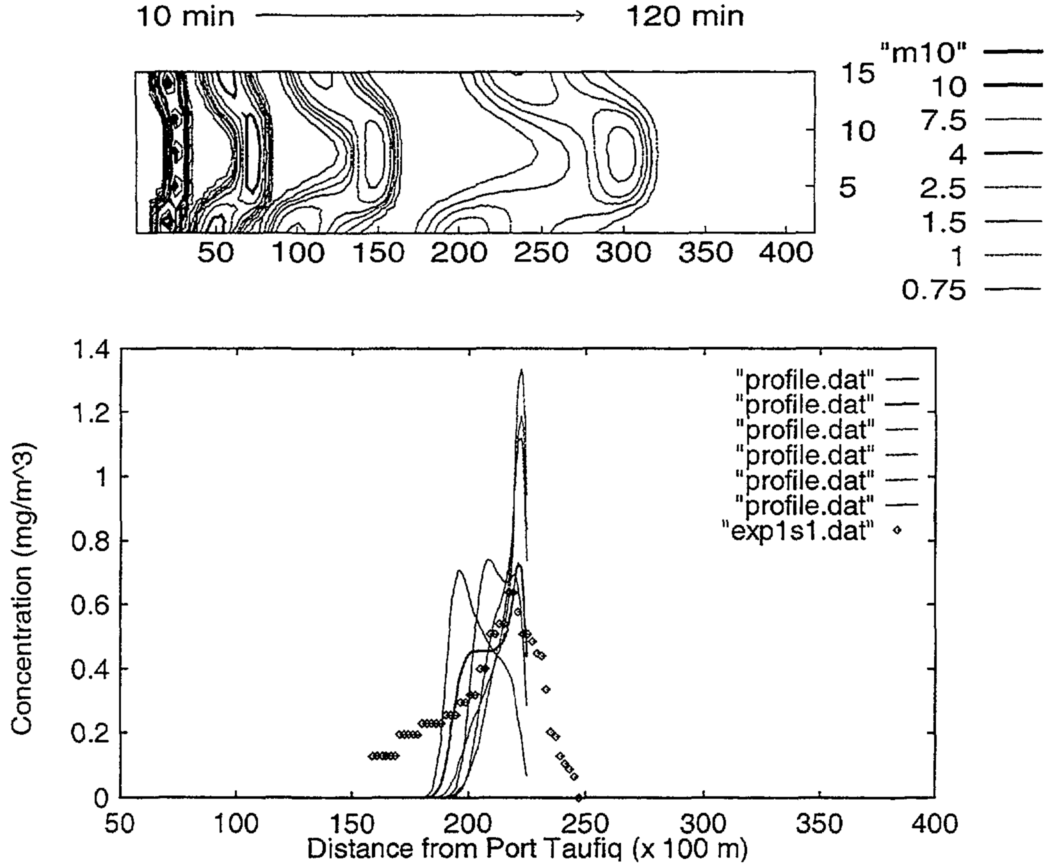

FIG 1 Simulation of the time and spatial evolution of the plume during the first tracing experiment. X and Y coordinates are grid positions, with grid length of 21 m, and Sallufa station corresponds to x=5 (km 146.2). The contour-lines for concentrations have units of mg/m^3. The plume moves northwards (positions at time 10, 30, 60 and 120 minutes after injection). The second figure shows a comparison between the measured and the computed concentrations of rhodamine B (these last along several longitudinal sections of the canal), at t= 170 minutes after injection.

Acknowledgements

We are indebted to all the colleagues from the NCNSRC, in Cairo, who participated in the IAEA Project, specially to Dr M.S. El-Tahawy, and to Dr A. Plata, from CEDEX, in Madrid. We also thank the collaboration of the Suez Canal Authority.

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IAEA-SM-354/54P

INFLUENCE OF TIME AND SPACE RESOLUTION ON DISPERSION OF RADIONUCLIDES AND RADIOECOLOGICAL ASSESSMENT IN THE MARINE ENVIRONMENT

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In connection with radiological assessments, it is necessary to cover large distances (> 1000 km) and long time-scales (centuries or millenniums). Another feature of the radiological assessment of discharges of radionuclides to the marine environment is the necessity to investigate simultaneously the processes of transport, transfer and uptake of radionuclides from sources to doses for man. Box-model analysis is available for these purposes [1].

The general assumption for box modeling about instantaneous mixing in each box, leads in practical calculations to instantaneous mixing in the whole of oceanic space. To improve the model, a box model which still describes a box structure with uniform mixing in all boxes, but also includes dispersion of radionuclides during time was created. This gives a better and more realistic/physical approach compared to traditional box modeling. The present version of the model keeps the options for global modeling, but also has elements of more local/regional models. This feature of the model could be significant for evaluating the role of local features (for example, rivers and estuaries) for dose assessment [2].

The equations of the transfer of radionuclides between the boxes of the model are of the form:

$$\frac{dA_i}{dt} = \sum_{j=1}^{n} k_{ji} A_j - \sum_{j=1}^{n} k_{ij} A_i \gamma(t \geq T_j) - k_i A_i + Q_i, \quad t \geq T_i$$

$$A_i = 0, \quad t < T_i$$

where $k_{ii}=0$ for all i, A_i and A_j are activities (Bq) at time t in boxes i and j, k_{ij} and k_{ji} are rates of transfer (y^{-1}) between boxes i and j, k_i is an effective rate of transfer of activity (y^{-1}) from box i taking into account loss of material from the compartment without transfer to another, for example radioactive decay, Q_i is a continuous source of input into box i (Bq y^{-1}), n is the number of boxes in the system, T_i is the time of ability (the first times when box i is open for dispersion of radionuclides) and γ is an unit function

$$\gamma(t \geq T_i) = \begin{cases} 1, & t \geq T_i \\ 0, & t < T_i \end{cases}$$

The times of ability T_i are calculated as a minimized sum of the weights for all paths, from the initial box with discharge of radionuclides to the box i on the oriented graph $G=(V, E)$ with a set V of nodes, v_j, correspondent to boxes, and a set E of arcs, e_{jk}, corresponding to the transfer possibility between the boxes j and k. Every arc, e_{jk}, has a weight, w_{jk} which is defined as time required for the transfer of radionuclides immediately from box j to box k (without any way through other boxes). Weight, w_{jk}, is considered as a discrete function of the water fluxes between boxes, geographical information and expert review. It should be stressed that we do not include new additional parameters in the model but only try to organize basic data as well as possible. Therefore the general uncertainty of calculations according to the present model will not increase in comparison to the traditional approach.

According to the system of equations a set of submodels with the same box structure, but with different graph structures corresponding to discharge of radionuclides from Sellafield, La Hague, Novaya Zemlya Bay, Obskaya Guba and Barents Sea was created.

The comparison of times of ability according to calculations on the graph structure with xperimental and modeling study of transit/resident times [3,4,5] indicates a satisfactory agreement etween values.

Selected results for calculated doses to man from the present model and from the model described n [4] for one thousand years are shown in Table I. Calculations corresponded to a unit (1 TBq) discharge f radionuclides into Obskaya Guba. Comparison of doses for man in the Table I indicates difference for lose assessment for some radionuclides and locations of discharge of radionuclides.

ABLE I. COMPARISON OF WORLD COLLECTIVE DOSES FOR 1000 YEARS FROM 1TBq ISCHARGE OF RADIONUCLIDES TO THE OBSKAYA GUBA, man Sv

adionuclides	Present model	[4]
^{0}Co	1.5E-4	2.1E-4
^{37}Cs	3.0E-3	3.9E-3
^{0}Sr	4.7E-4	5.7E-4
^{41}Am	2.9E-3	6.1E-2
^{39}Pu	3.0E-2	2.2E-1

Calculations of the doses to man for different radionuclides, indicate that the differences between he results of calculations, as well as concentration of radionuclides, could be up to an order of magnitude n comparison with traditional modelling.

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XA9951973

RECONSTRUCTION AND OUTLOOK OF THE RADIONUCLIDE TRANSPORT IN THE MEDITERRANEAN SEAS CHAIN

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A set of models was developed to reconstruct and predict in 1960-2010 the ^{137}Cs contamination in the system of Mediterranean seas that was result of the testing of nuclear weapons and the Chernobyl accident. It incorporates the submodels of the Black Sea, Azov Sea, Marmara Sea, Western and Eastern Mediterranean. The one-and-half-dimension multilayer LAgrangian model of TOXicant transport LATOX [1] describes the horizontally averaged fields of temperature, salinity and tracer concentration in the seas proper. The vertical hydrological structure of water body was approximated by set of homogeneous layers. The number of layers and their thickness are varied in the time and depend on preceding course of the process. The layers can move in vertical direction accordingly to the mass balance ("lagrangian layer"). The system of layers includes surface mixed layer that is under direct atmosphere influence, internal and bottom layers. The simple models of hydraulically controlled straits were applied to Bosphorus, Dardanelles, Sicily strait and Gibraltar. An empirical relation was used for shallow Kerch strait. The model is forced using time series of the wind, temperature and freshwater influx.

The results of simulation of ^{137}Cs concentration in the surface layer of the Black Sea were compared with observed data. The model computes quite realistic the tracer evolution. The calculated ^{137}Cs activity in the Azov Sea water column in 1985 was 22 Bq m^{-3}. It increased up to 280 Bq m^{-3} at May 1986 and falls to 38 Bq m^{-3} in 1987 that is in good agreement with observed [2] range 20-40 Bq m^{-3} in 1987. The model predicts the decay of activity down pre-Chernobyl level in 2010. The simulation results for the West and East Mediterranean are presented in Fig. 1. The calculations also fit observations. The noticeable seasonal effects, connected with deep winter convection, were pronounced, notably in the Eastern Mediterranean, where winter convection reaches the bottom. The result was the disappearance of the Chernobyl signal in surface waters of Mediterranean Sea proper. According to [3] the total amount of ^{137}Cs of the Black sea in 1977 was 1.37± 0.30 PBq and 0.18 PBq in the water column and bottom deposition, respectively. The computed amount was 1.15 PBq in the water column. Nikitin et al. [4] estimated the increase of ^{137}Cs in the Black sea in 1986 as 1.66 PBq, whereas predicted value was 1.55 PBq. An exchange through straits results in the difference in the temporal evolution of total amount of ^{137}Cs in Western and Eastern Mediterranean. The tracer caught in the Western Mediterranean through Gibraltar strait and by atmosphere fallout was transported to the Sicily strait by the upper layer current. Thereafter it entered the Eastern Mediterranean, mixed by winter convection and returned to the Western Mediterranean by bottom undercurrent through the Sicily strait. Therefore the ^{137}Cs amount in the Western Mediterranean was remained almost constant from 1980 as distinct from the Eastern Mediterranean. The tracer transport through the Kerch strait in 1960-1994 was 8.7 TBq (6% of fallout) and through the Bosphorus was 0.4 PBq (7% of fallout). The exchange through the Sicily and Gibraltar straits were more important in the radionuclide budget. The transport through Gibraltar in 1960-1985 was 4.7 PBq (40% of fallout).

The presented results showed the capability of model to reconstruct the redistribution of radionuclide in the complex systems of seas as well as usefulness using of isotope tracer in a calibration and evaluation of the circulation models. This contribution is a brief resume of the author paper [5].

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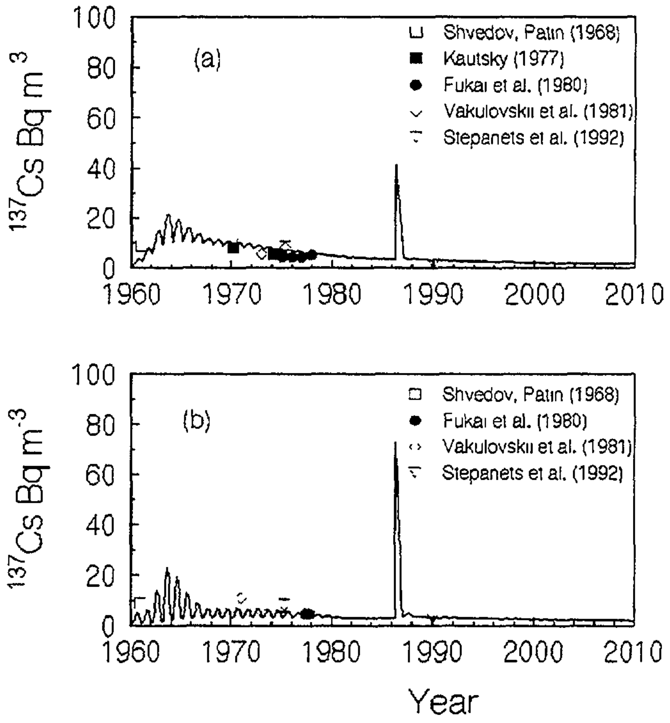

1. Comparison of the results of simulation with observed variations of ^{137}Cs concentration in the surface layer of the Western (a) and Eastern (b) Mediterranean (Maderich ,1998).

IAEA-SM-354/58P

A RADIOLOGICAL ASSESSMENT OF THE NUCLEAR REACTORS WITH SPENT FUEL WHICH HAVE BEEN SCUTTLED IN THE KARA SEA

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In 1995 the European Commission initiated a study to evaluate the radiological consequences of the marine reactors that were scuttled in the Kara Sea and the associated uncertainties. The study considered objects located in bays on the east coast of Novaya Zemlya (OK-150 in Tsivolki bay, NS-285 and NS-901 in Abrosimov bay, and NS-601 in Stepovogo bay) and in the Novaya Zemlya Depression. The detailed findings are published by the Commission [1].

The calculations of radionuclide inventories are based on information on the operating histories of the nuclear reactors. The overall uncertainty associated with the inventories of fission products and actinides for the OK-150 fuel is estimated to be less than 20%. A similar value applies to the fission products in the submarine fuel but, due to the higher enrichment, the actinide uncertainty is assessed at a factor 3. The barriers employed to retain the activity are stainless and carbon steels, furfurol, concrete and bitumen. Experimental data were used to evaluate the corrosion rates taking into account the effects of marine organisms and the galvanic coupling of stainless and carbon steels.

The dispersion of radionuclides in the bays of Novaya Zemlya, the Kara Sea and along the mainland coast was evaluated using the THREETOX and the COASTOX models developed by CCUAS. The THREETOX model simulates 3-D hydrodynamic fields, suspended sediment and radionuclide transport in the water. Local-scale modelling was applied to estimate the radionuclide concentrations in the water and top layer of bottom sediments in the Novaya Zemlya bays as a function of time. Regional-scale modelling provided radionuclide concentrations in the water and sediments of the Kara Sea with input of radionuclides from the Novaya Zemlya Depression and the Novaya Zemlya bays. The two-dimensional model COASTOX provided high-resolution simulation of the distribution of radionuclides in the near-shore zone, taking into account the joint effect of waves and currents on the radionuclide transport and transfer in the bottom boundary layer. This model was used to provide a basis for the assessment of doses to critical groups.

Short- and long-range dispersion was calculated using a box model. The model is developed for the assessment of the radiological consequences of releases of radioactive material to the marine environment covering the Arctic Seas and the North Atlantic including European coastal waters. The model simulates dispersion of radioactivity in the water due to advective transport including mixing from wind and tidal forces. Association of radionuclides to suspended sediment material is taken into consideration in addition to subsequent transfer to sediments through particle scavenging. Further transfer of radionuclides between the water column and the sediments include diffusion, bioturbation and resuspension. From specified inputs of radioactivity to the marine environment the model calculates time-dependent concentrations in seawater and sediments. These data are used to calculate doses to man from a range of exposure pathways: ingestion of fish, crustaceans, molluscs, seaweed; external exposure on beaches; in halation of sea spray and resuspended beach sediments. Doses are calculated to individual members of critical groups and to populations.

The critical groups include hypothetical military personnel on Novaya Zemlya and people in new towns of 50,000 inhabitants to support the gas industry on the Yamal and Taymur peninsulas.

The best-estimate total collective dose was calculated to 0.8 manSv when integrated over 10,000 years with relative contributions by nuclide and pathway as shown in Figure 1.

The best-estimate maximum dose rate to any potential residential group is 0.02 μSv y^{-1} in 1970 due to Fe-55 to the new town on the Yamal peninsula and the maximum dose rate to personnel at Tsivolki Bay is derived to be 0.5 μSv y^{-1} in the year 3350. These values are significantly below the value

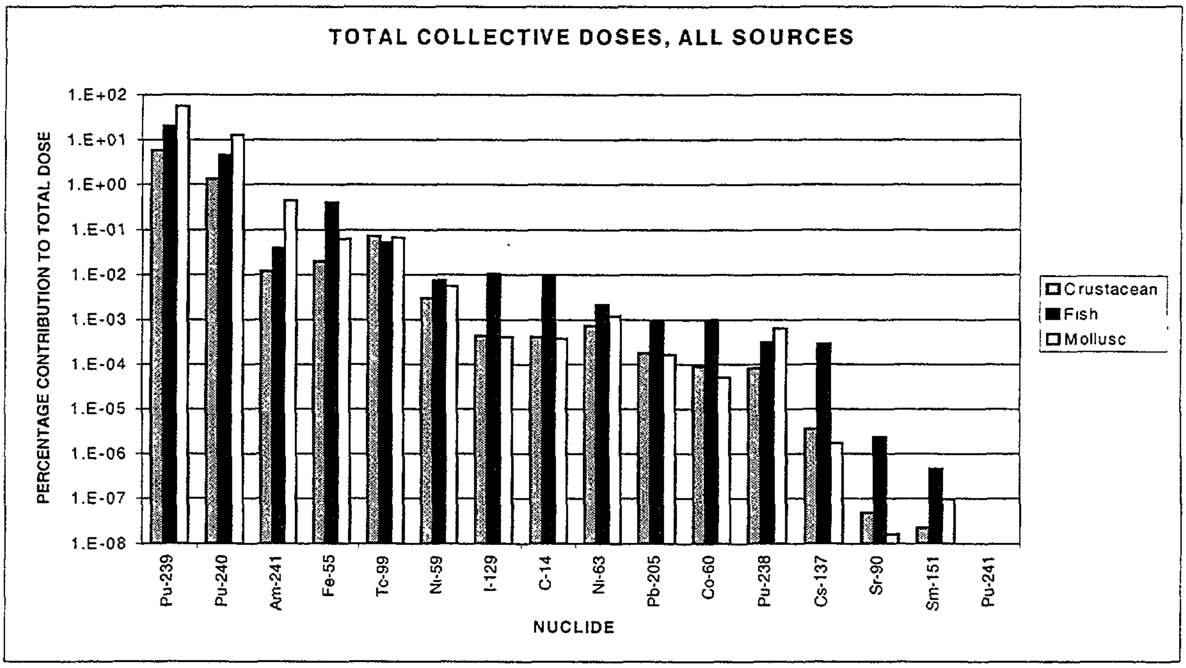

FIG. 1. Relative contributions (per cent) by nuclide and pathway to the collective dose from all sites (marine pathways only).

of 10 μSv y^{-1}, which is the lower limit of dose rates that are considered to be of regulatory concern by the IAEA [2] and the 1996 Euratom Directive [3]. The doses due to other scenarios are of the same magnitude as the above although the doses due to the plutonium isotopes will occur about 1000 years earlier in the worst-case scenarios.

The best-estimate collective dose is less than the value of 1 manSv, which is considered to be the lower limit of regulatory concern by the IAEA [2] and the 1996 Euratom Directive [3]. This may be compared with the annual collective dose to the world's population from naturally occurring polonium-210 in the ocean, which is estimated in other studies to be four orders of magnitude higher.

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DISPERSION OF RADIONUCLIDES POTENTIALLY RELEASED FROM THE ATOLLS OF MURUROA AND FANGATAUFA TO NEIGHBORING ARCHIPELAGOS

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In the framework of IAEA's Study of the Radiological Situation at the Atolls of Mururoa and Fangataufa [1], a special interest was devoted to the assessment of present and potential radiological doses to human populations in the South Pacific, particularly those inhabiting the nearest islands. Since seafood constitutes an important fraction of the islanders diet [2], the marine dispersion from the atolls and the transfer of radionuclides through the marine food-chain to man has been the object of a number of studies and publications [2, 3, 4].

This paper presents a compartmental model developed to simulate dispersion of radionuclides released to the ocean from the atolls of Mururoa and Fangataufa on a scale of 3000 x 1700 km (15° to 30° S latitude, 130° to 160° W longitude), including the Tuamotu, Cook, Society, Gambier and Austral archipelagos. The horizontal resolution of the model is finer (0.5° x 0.5°) in the region of the atolls and to the nearest inhabited island (Tureia) and coarser (5° x 5°) beyond a range of 200 km from the atolls. The vertical structure is based on the analysis of flow-fields generated by the numerical model of the Pacific and Indian Oceans of Masumoto and Yamagata [5], and includes 3 water layers. Monthly values of the exchanges of water between the compartments are evaluated by spatially integrating flows obtained on the basis of monthly snap-shots of velocity fields predicted by the Masumoto and Yamagata model. The model also includes sediment-water interaction. The finer short-range model resolution permits to better simulate dispersion in the vicinity of the atolls, where steeper concentration gradients can be expected, and also to differentiate between the two atolls as sources. In the intermediate range, seasonality has been shown to have important effects, therefore

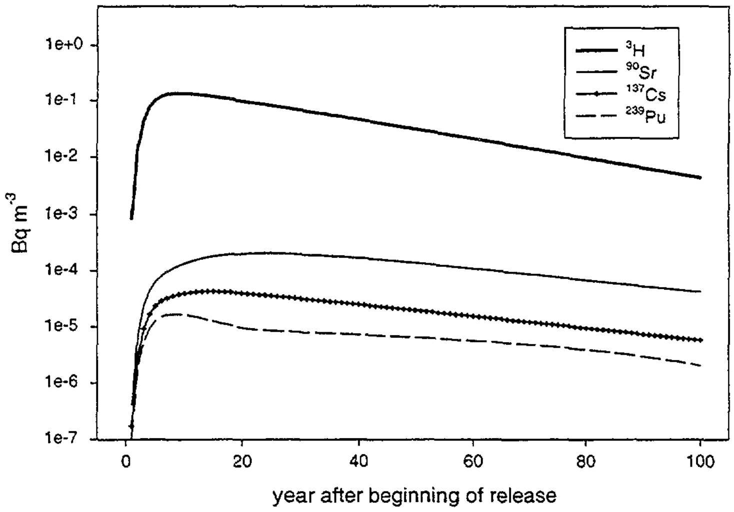

FIG 1. Annual mean concentrations of radionuclides averaged over the top 450 m layer of water at Tahiti. The release of radionuclides from the Atolls of Mururoa and Fangataufa takes place according to the normal release scenario given in [1] for a 100 y time-scale.

the model has been designed to reproduce monthly flow patterns by sequentially employing 12 sets of exchange coefficients, each of them characterizing circulation patterns and volume flows for a given month.

Simulations were performed for dispersion of ^{3}H, ^{90}Sr and ^{137}Cs on a time-scale of 100 years and for ^{239}Pu over 10,000 years. The release-rate functions considered were those corresponding to the source terms calculated by the Working Group 4 of the IAEA Study [1] for various scenarios. Predictions of time-dependent radionuclide concentrations were obtained for a number of 88 water compartments and 20 sediment compartments. Model predictions for concentrations of ^{3}H, ^{90}Sr, ^{137}Cs and ^{239}Pu in seawater at Tahiti are illustrated in Fig.1 for the normal release scenario in [1], which assumes the release to start in 1980. For the same scenario, the evolution of predicted ^{239}Pu concentrations over the longer time-scale at several locations in the South Pacific is shown in Fig.2. Maximum concentrations predicted are below present–day background levels measured in the region [1, 2]. Resulting individual dose-rates from consumption of seafood, calculated on the basis of generic values of the concentration factors [6] are negligibly small as compared to those from natural ^{210}Po.

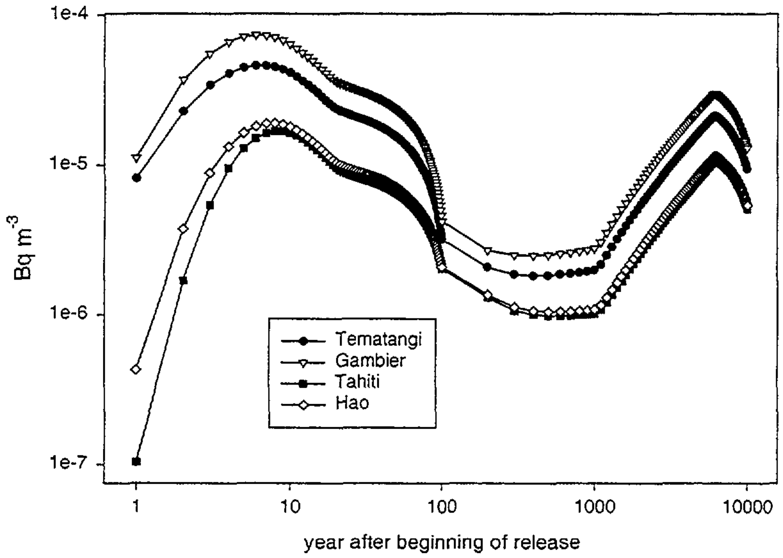

FIG 2. Annual mean concentrations of ^{239}Pu averaged over the top 450 m layer of water at various inhabited locations in the South Pacific for the long-term normal release scenario given in [1].

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PREDICTIONS OF RADIONUCLIDE DISPERSION IN SEAWATER AROUND THE MURUROA AND FANGATAUFA ATOLLS

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The International Atomic Energy Agency has conducted a study, requested by the Government of France, to assess the radiological situation at the atolls of Mururoa and Fangataufa in French Polynesia [1]. In the framework of the study, dispersion of radionuclides in surface seawater in a regional scale has been predicted for several source term scenarios using an equidistant-grid compartmental model

The equidistant-grid compartmental model used in this study was developed for regional scale modelling of discharges from a spent nuclear fuel reprocessing plant in Japan [2]. For this study, the region of interest is defined to be 10 to 30° S and 125 to 155° W (roughly 2,200 km × 3,100 km). Fig.1 shows the area which is centered on the atolls and includes the Tuamotu Archipelago and the Society, Austral and Gambier Islands.

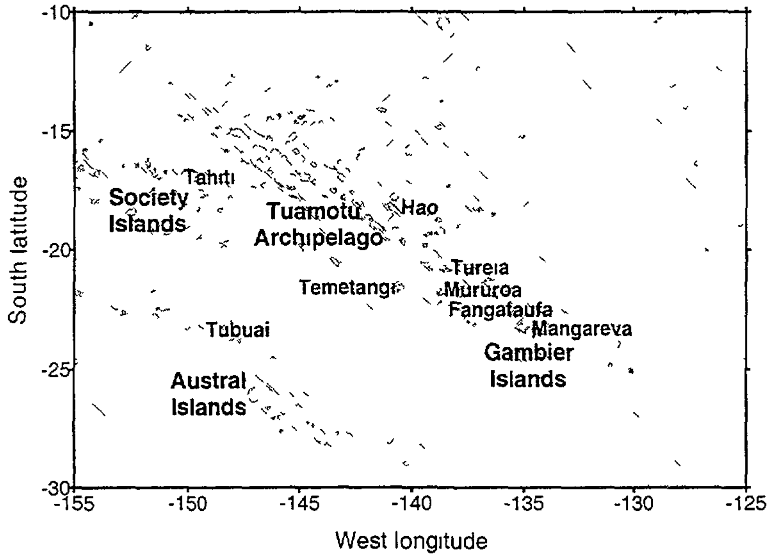

FIG.1 Regional domain for the equidistant-grid compartmental model

The model domain is horizontally divided into compartments of 1° in latitude and longitude (approximately 110 km × 110 km). The number of compartments is 600 (20 × 30). The radionuclide concentration in each compartment is estimated using a simple model, in which the effect of the thermocline is taken into account. It is assumed that the concentration is uniform through the water column from the surface to a depth of the thermocline and that radionuclides are not transferred down below the thermocline by diffusion but by sedimentation. A depth of the thermocline is defined 400 m.

Ocean current data in the original model were based on calculation of the geostrophic current using the measured data of temperature and salinity. However, the current data of Masumoto and Yamagata [3] are used for this study. This database has a resolution of 0.5° in latitude and longitude with 20 layers from the surface to the bottom. A total of 12 data sets are available, each of which contains monthly-averaged snapshot velocities (u, v, w) at all grid points. For the model used here, annual-averaged values are calculated for each compartment of 1° of both latitude and longitude and for a layer from the surface to a depth of the thermocline

The bathymetry data were provided by Hamburg University Volume, vertical cross section and average depth for each compartment are calculated by linearly interpolating the depth data. The transfer of radionuclides between compartments is estimated by summing components due to the ocean current and eddy diffusion. The eddy diffusion coefficient of 100 m^2/s is used here over the entire domain.

Model simulations are conducted using 3 source term scenarios : i) instantaneous release following a hypothetical slide in the carbonate zone, ii) time-dependent current release from the lagoons combined with a future release from underground sources, and iii) periodical and instantaneous release of plutonium simulating a severe storm event every ten years. Concentrations of ^{3}H, ^{90}Sr, ^{137}Cs and $^{239,240}Pu$ in surface water are estimated near several inhabited islands (Fig.1). It is assumed that all radionuclides are released from Mururoa into the surface water.

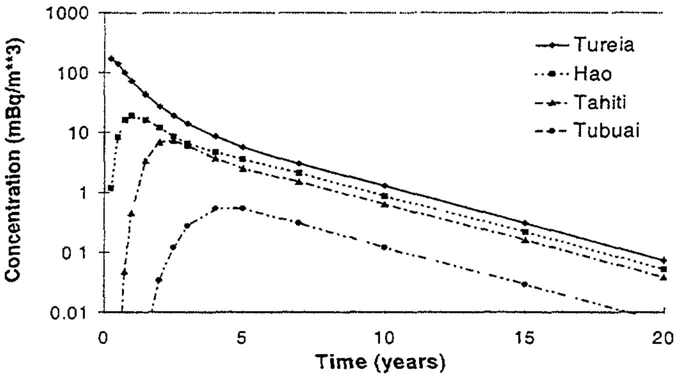

Fig.2 Concentrations of Pu-239,240 following a hypothetical slide in the carbonate zone

In a disruptive event scenario, only the predicted results of $^{239,240}Pu$ are above the present background level for the surface waters in the South Pacific Ocean : 100-200 Bq/m^3 for ^{3}H, 1-2 Bq/m^3 for ^{90}Sr, 2-3 Bq/m^3 for ^{137}Cs and 1-4 mBq/m^3 for $^{239,240}Pu$ [4]. Fig.2 shows the time-dependent concentrations of $^{239,240}Pu$ in surface water near four inhabited islands. The total amount of a plutonium release is 10 TBq. The time of a peak concentration and its value are related to the distance of the islands from Mururoa, i.e. the longer the distance is, the longer the time of the peak concentration is and the lower its value is. The concentration field shows the pattern that the water is mixed in the higher and lower latitudes and transported rapidly to the west in the northern part of the South Pacific Ocean and to the east in the southern part, faster than the center of mass.

A time-dependent release scenario gives the results that all the concentrations are well below the background levels. For a storm scenario, the first three peak concentrations of $^{239,240}Pu$ at the nearest island (Tureia) are comparable with the background level.

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PLUTONIUM-241 IN SEAWATER OF THE NORTHWEST EUROPEAN SHELF SEAS 1989-1993

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This poster contributes to the knowledge about the levels and distribution of ^{241}Pu in seawater in the North Sea and adjacent European shelf seas during the period 1989-1993. The controlled release of low-level radioactive waste from European nuclear fuel reprocessing plants in the UK (Sellafield, Dounreay) and France (La Hague) has led to a widespread contamination of the northeast North Atlantic and its adjoining shelf seas, Sellafield being the main contributor. Within the numerous nuclides released into the marine environment, results of ^{241}Pu have been published rather sparsely. ^{241}Pu has a half-life of 14.35 years and decays to ^{241}Am. The documented principal sources of ^{241}Pu in the marine environment are atmospheric fallout from nuclear weapon tests during the sixties and discharges from the Sellafield reprocessing plant. From the nominal total activity of 191 PBq ^{241}Pu, which was injected into the environment (3,4,5) up to 1993, a substantial part of 11% was contributed by Sellafield, mainly in the seventies. From the 21.5 PBq released by the Sellafield plant up to 1993, less than 1% was released during the period of this study. The application of the ^{241}Pu/^{239,240}Pu activity ratio allows to distinguish between fallout and reprocessing releases. Decay corrected to 1993, the ratio is calculated to be 6.3 (fallout) and 14.2 (Sellafield), respectively. In contrast, the release ratio during the period 1989-93 was steadily >30.

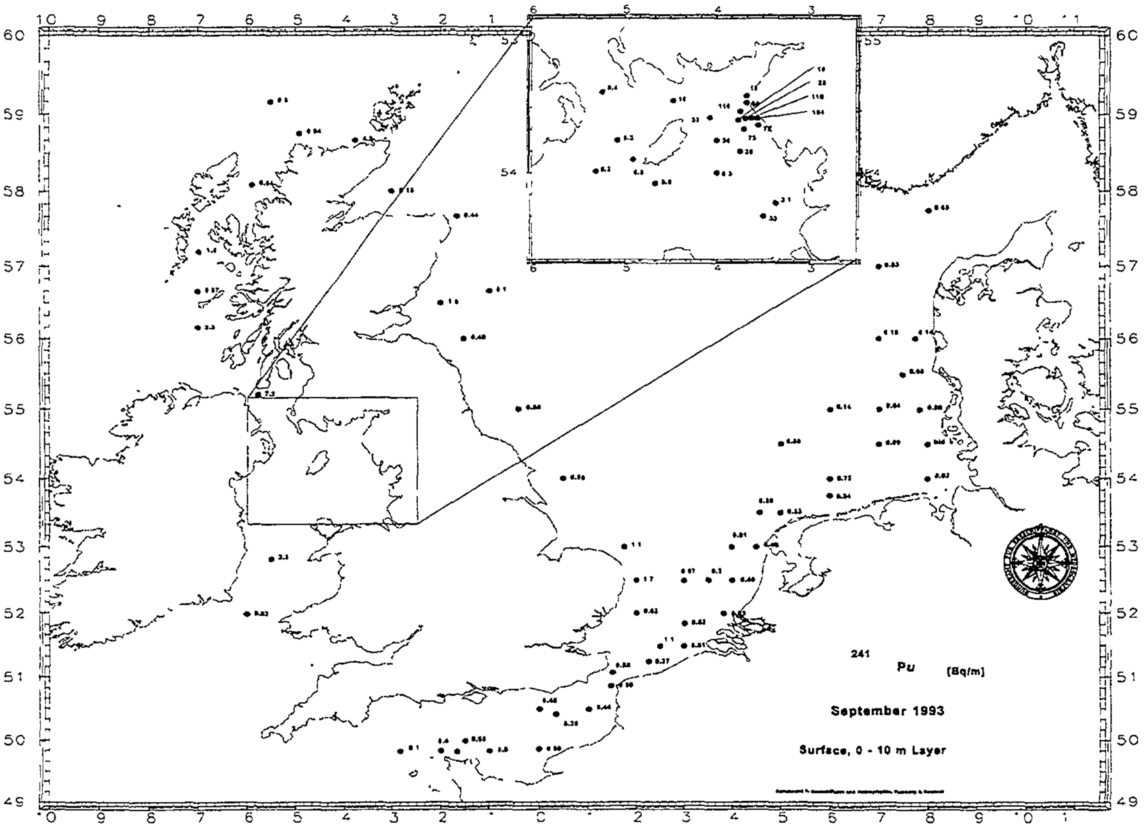

FIG. 1. Examplary distribution of ^{241}Pu in unfiltered seawater in the North Sea and Irish Sea in 1993.

The BSH conducts regular research cruises to monitor man-made radionuclides in the North Sea and the adjoining shelf seas. Generally once per year, unfiltered seawater samples of 50 or 100 l are collected and analysed for transuranium elements as ^{238}Pu, ^{239,240}Pu and ^{241}Am. During the analytical process which is described in detail elsewhere(1), ^{241}Pu is chemically separated and electroplated on stainless steel discs along with the other Pu nuclides. Due to its half-life a substantial amount of ^{241}Pu has decayed to ^{241}Am after a period of about 5 years and allows recounting. The ^{241}Am (main alpha line at 5.486 MeV) ingrowth adds to the already existing ^{238}Pu (5.499 MeV) alpha line. For a detailed discussion of this procedure see ref.2. The 1σ uncertainties of the method are typically around 15 % (range 5-30 %).

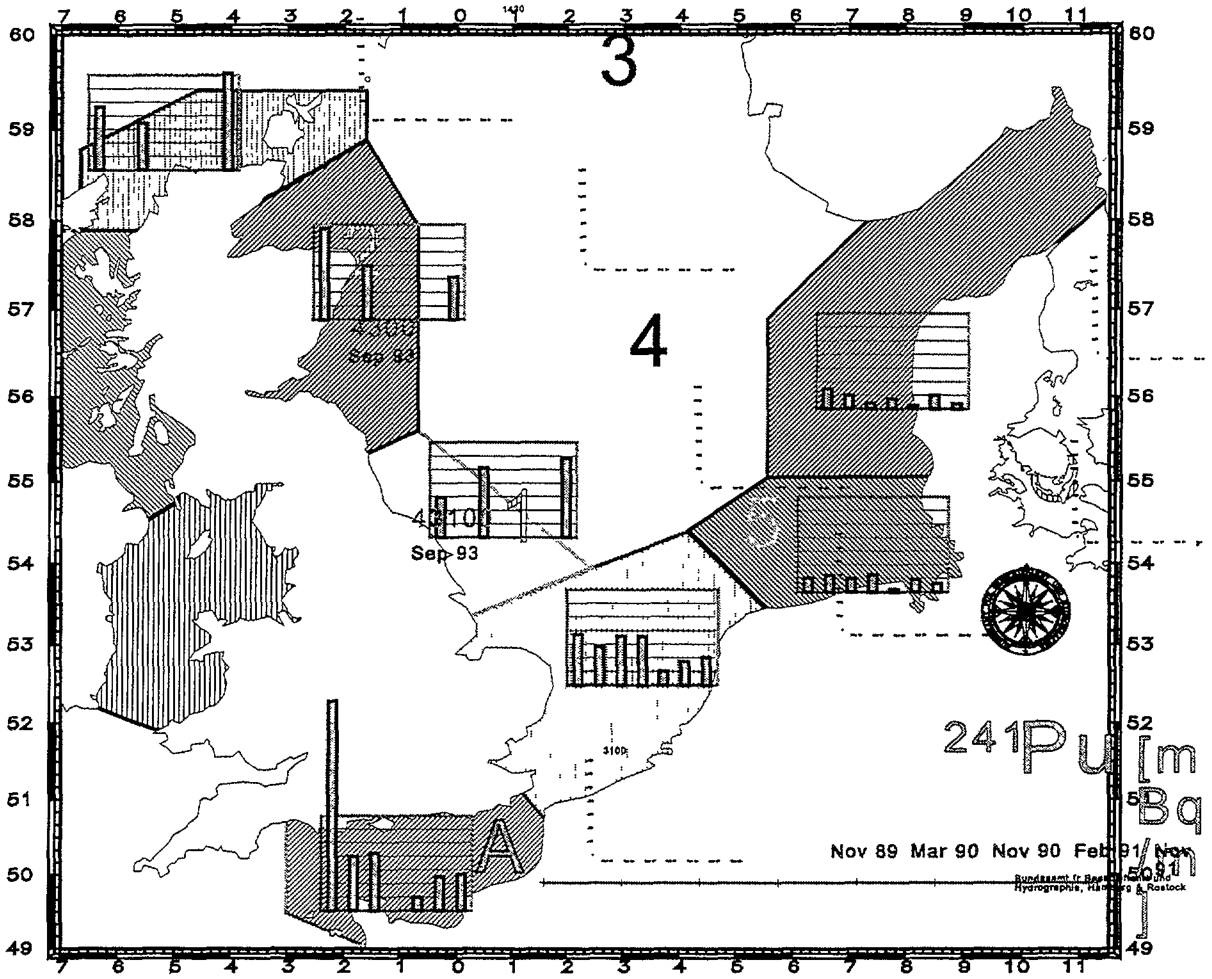

FIG. 2. Time series of mean 241Pu activity concentrations in unfiltered seawater in Northwest European Shelf Seas 1989-1993

We found high levels of ^{241}Pu activity concentrations both for Sellafield and for La Hague labelled waters. Activity concentration levels span from 0.03 to 194 Bq/m³ (see Fig. 1), the latter not corresponding with the amount of releases during 1989-93. Based on 263 determinations of 241Pu in unfiltered seawater in 1989-1993, time series of arithmetic means in various parts of the Northwest European Shelf Seas are presented in Figure 2. Whereas we have no proof in the case of the La Hague plant, as the source term of this establishment is not published, our results demonstrate clearly that the Pu activities found here in Sellafield labelled waters are not dominated by releases during the study period. Instead, the mean ^{241}Pu/^{239,240}Pu activity ratio found in seawater of the Irish Sea, the waters around Scotland and the central North Sea is ~15, which corresponds very well with the total ^{241}Pu/^{239,240}Pu inventory released from Sellafield. In contrast, very few samples of the whole study show a ^{241}Pu/^{239,240}Pu activity ratio, which is of fallout origin.

As the variability of the 241Pu concentrations found in this study is at least one order of magnitude higher than that of conservative radionuclides (^{137}Cs, ^{125}Sb, ^{90}Sr, ^{99}Tc; ref. 6) in the same area and time period, we conclude that transport of suspended or resuspended particles (7) play an important role in the distribution mechanism. The ^{241}Pu/^{239,240}Pu activity ratios found here establish the seabed of the Irish Sea as the principal source of Pu in the Irish Sea and the central North Sea in the period of this study. Combined with recent findings about the widespread occurrence of Pu derived from reprocessing activities in the North Atlantic (1), the knowlegde of comparatively high concentrations of ^{241}Pu in European waters form a basis for estimations of the occurrence of ^{241}Am far afield from reprocessing sites.

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IAEA-SM-354/64P

CAESIUM-137 IN BALTIC SEA SEDIMENTS SINCE THE CHERNOBYL ACCIDENT

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The Baltic Sea was the sea most affected by the Chernobyl accident, because the first radioactive clouds from Chernobyl travelled north and caused high deposition in the Baltic Sea region [1]. The distribution pattern of Chernobyl-derived ^{137}Cs in the catchment area of the Baltic Sea was very scattered, with the highest deposition values occurring in the areas surrounding the Gulf of Bothnia and the Gulf of Finland. The highest ^{137}Cs concentrations in bottom sediments also occurred in these gulfs, but the scattered nature was further emphasized as a consequence of river discharges, sea currents and different sedimentation rates on hard and soft bottoms. Our first attempts to estimate total ^{137}Cs in Baltic Sea sediments were made in the early 1990s [2,3]. The present report contains a revised estimate based on a larger quantity of sediment data than the previous estimates.

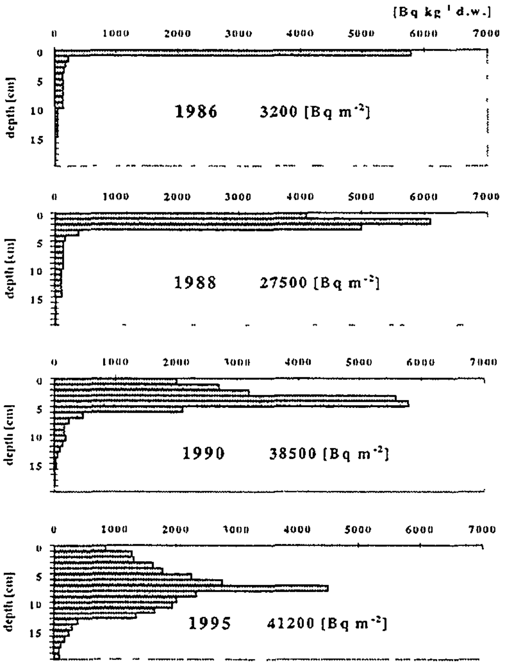

FIG.1. Vertical distribution and total amount of ^{137}Cs in 1986-1995 at a coastal station on the Gulf of Finland.

TABLE I. TOTAL AMOUNTS OF ^{137}Cs [Bq m^{-2}] IN SEDIMENTS OF DIFFERENT SUB-BASINS AND THE NUMBER OF SAMPLING STATIONS. (*=SELECTED OBSERVATIONS USED IN CALCULATIONS)

	Gulf of Finland	Bothnian Bay	Bothnian Sea	Baltic Proper
mean*	18600	8700	34600	2100
median	15200	8600	35100	1900
max	78100	98700	116300	10200
min	1400	4300	7800	600
Station	79	8	12	30

Sediment data were collected in 1993-1997 by STUK and FIMR during voyages of the R/V ARANDA. The total number of sampling stations was 129 (180 cores). The samples were taken with a GEMINI Twin Corer and ^{137}Cs activity was measured gammaspectrometrically. The activity concentrations were time-corrected to April 26, 1996. The mean content of ^{137}Cs [Bq m^{-2}] in the soft and hard sediment of various sub-basins was multiplied by the area of soft and hard bottom in each [4] measured planimetrically from maps of Quaternary deposits in the Baltic Sea [5]. An empirical ratio of 1:20 was used to calculate ^{137}Cs values for hard bottoms [2]. Positively skewed distribution of the data led in some cases to a strong influence of individual results on mean values. In these cases some stations or a certain portion of maximum and minimum values were omitted because of statistical considerations.

The results show that Chernobyl-derived caesium has continued to sink to the bottom of the sea during the 1990s (Fig.1). The proportion represented by the Bothnian Sea is clearly dominant in the total Baltic Sea inventory of ^{137}Cs (Fig. 2, Tables I and II). The highest amounts of ^{137}Cs were found in the northern Bothnian Sea (116 300 Bq m^{-2}) and in the southernmost area of the Bothnian Bay (98 700 Bq m^{-2}), but the areal representativeness of these maxima remained unverified in the present study. According to our new estimate, the total value for ^{137}Cs in sediment was 2.14 PBq in 1996 (Table 2). This value is about double our estimate from 1991 and is almost equal to that estimated for Baltic Sea water by the HELCOM/MORS Group [6]. The marked increase in the estimated value resulted from increased information on ^{137}Cs in sediments and the fact that Chernobyl-derived caesium has continued to sink to the bottom of the sea. Nevertheless, more information is still needed about the distribution pattern of ^{137}Cs in certain sub-basins, e.g. the northern Bothnian Sea.

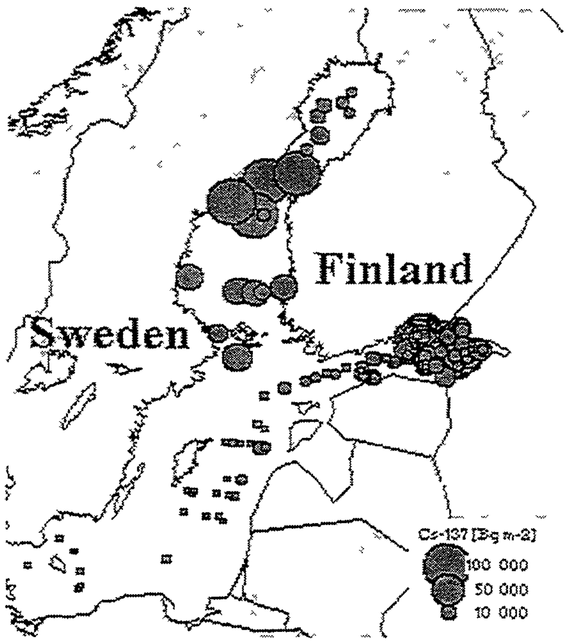

FIG.2. Total amounts of Cs-137 [Bq m^{2}] at sampling stations in different parts of the Baltic Sea.

TABLE II. INVENTORIES OF ^{137}Cs IN DIFFERENT SUB-BASINS OF THE BALTIC SEA BASED ON SURFACE AREAS OF SOFT AND HARD BOTTOMS [km^2] IN EACH

Sea area	Bottom type	[km^2]	1991 inventory [Bq]	1998 inventory [Bq]	Portion of the total in 1998
Bothnian Bay	soft	16000	4.80E+13	1.39E+14	
	hard	21000	3.15E+12	9.12E+12	
	soft+hard	37000	5.12E+13	1.48E+14	7 %
Bothnian Sea	soft	40000	6.64E+14	1.38E+15	
	hard	39000	3.24E+13	6.74E+13	
	soft+hard	79000	6.96E+14	1.45E+15	67 %
Gulf of Finland	soft	16000	2.43E+14	2.98E+14	
	hard	14000	1.06E+13	1.30E+13	
	soft+hard	30000	2.54E+14	3.11E+14	15 %
Baltic Proper	soft	106000	2.23E+14	2.20E+14	
	hard	122000	1.28E+13	1.27E+13	
	soft+hard	228000	2 36E+14	2 32E+14	11 %
Baltic Sea	soft	178000	1.18E+15	2.04E+15	
	hard	196000	5.90E+13	1.02E+14	
	soft+hard	374000	1.24E+15	2.14E+15	100 %

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239+240Pu IN SETTLING PARTICLES ON THE EAST CHINA SEA CONTINENTAL MARGIN

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The transport process of $^{239+240}$Pu on the East China Sea continental margin was investigated by measuring the concentrations of $^{239+240}$Pu in settling particles. Mooring location of the sediment trap experiment is shown in Fig.1. Settling particle samples were collected at three observation stations (Stn.F-4, F-6, and F-8) by using sediment traps. The sediment trap mooring strategy at transect F line is shown in Fig.2. Three moorings of sediment traps were deployed on the continental shelf edge and slope from 26 October 1995 to 4 November 1995. Three conventional sediment traps were deployed at Stns. F-4, F-6, and F-8. Two sequential traps were also deployed on same mooring of Stn. F-4 at 502 m and 574 m depth. The sampling interval of F-4 sequential traps was 12 hours from 26 October 1995 to 4 November 1995. The activities of $^{239+240}$Pu were determined with an alpha spectrometer equipped with silicon surface barrier detectors and pulse height analyzer after chemical separations. 210Pb in settling particles was also analyzed via counting of the activity of 210Bi using a low-background beta counter.

Total mass fluxes from the shelf edge and slope in the Fall of 1995 range from 0.48 to 9.1, 1.2 to 5.9, and 9.7 to 23.3 mg/m2/day at Stns. F-8, F-6, and F-4, respectively.

Total mass fluxes show a general tendency to increase with depth, especially showing a very large increase at near bottom.

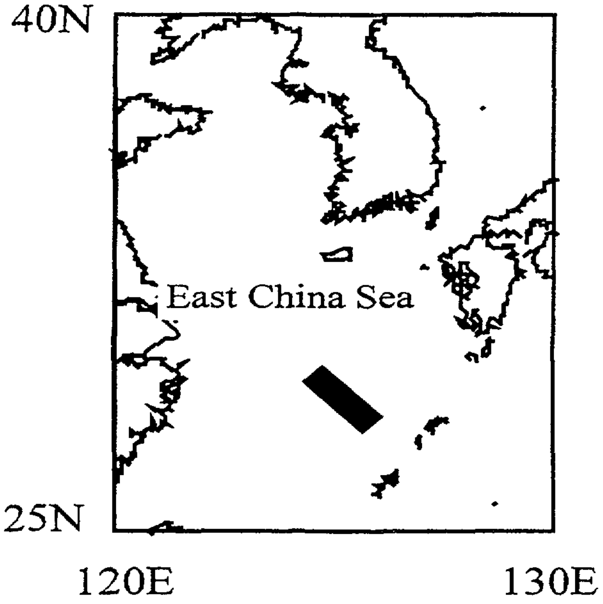

FIG. 1. Location of the sediment trap experiment.

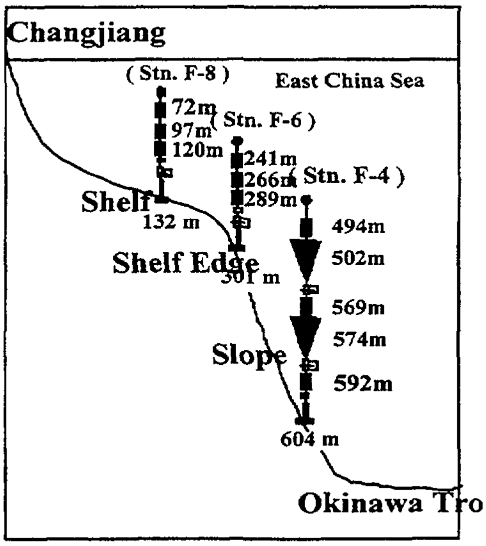

FIG. 2. Sediment trap mooring strategy For a short term deployment at Transect F.

Vertical profile of 239+240Pu concentrations in settling particles is shown in Fig.3. 239+240Pu concentrations increase with depth from 1.8 mBq/g at 97 m depth to 3.0 mBq/g at 120 m depth on the continental shelf edge (Stn. F-8) and range from 3 to 4 mBq/g below the depth of 120 m. Vertical profile of 239+240Pu fluxes is shown in Fig.4. There is a clear tendency for 239+240Pu fluxes to increase with depth at each stations. Highest 239+240Pu fluxes are observed in near-bottom at each stations.

210Pb concentrations in settling particles increase with depth from 0.70 Bq/g at 97 m depth to 1.35 Bq/g at 592 m depth. It could not be explained that these increases are due
to degradation of organic matter during the descent of settling particles and uptake of 210Pb by settling particles. 210Pb concentrations in surface sediments are lower than those of near-bottom samples. The large fluxes and increases of 210Pb with depth also could not be explained as coming from resuspension of surface sediments.

The large fluxes of 239+240Pu in the near-bottom traps and the increases of 210Pb concentrations in settling particles with depth may be attributable to lateral transport of undulated particles which slide down on the continental slope nepheloid layer.

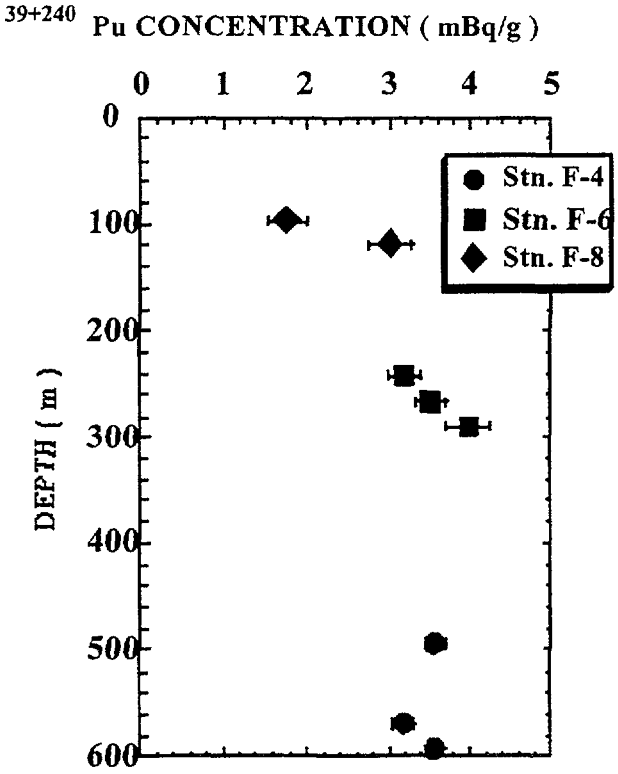

FIG. 3. Vertical Profile of Pu239+240 concetrations in settling particles.

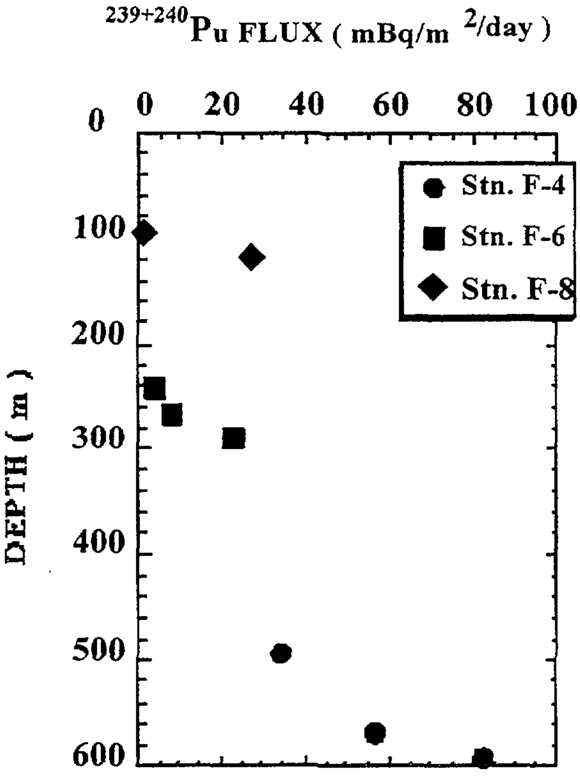

FIG. 4. Vertical profile of Pu239+240 Fluxes on the East China Sea continental margin.

IAEA-SM-354/66P

^{210}Po/^{210}Pb DISEQUILIBRIA IN THE SHELF EDGE OF THE EAST CHINA SEA

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The uranium-238 series radionuclides ^{210}Pb ($t_{1/2}$ = 22.3 yr) and its daughter ^{210}Po ($t_{1/2}$ = 138 days), are important tracers in the marine environment. They are especially useful for studies on material transport scavenging processes within relatively short times and on the mechanism of material transport from coastal zones to the open sea, because they are highly reactive to the particulate matter and is rapidly removal from the water column. In this study, we present measurements of ^{210}Po and ^{210}Pb concentrations in seawater and the calculated rates of removal of these radionuclides from the water column in the shelf edge of the East China Sea.

Seawater samples were taken at PN and F line during the MASFLEX (Marginal Sea Flux Experiment in the West Pacific) project cruises in the East China Sea (Fig.1). Since we analyzed unfiltered seawater, the data presumably represent the total concentration in seawater.

Vertical profiles of ^{210}Po and ^{210}Pb on October 95 in the East China Sea were shown in Fig. 2. The concentrations of ^{210}Pb in the Kuroshio Current region were higher than those in the coastal and shelf waters and the concentrations of ^{210}Po and ^{210}Pb decreased rapidly in the area from the Okinawa Trough to the East China Sea. The ^{210}Po deficiencies relative to ^{210}Pb were recognized in the surface and deep layer.

The inventories of ^{210}Po and ^{210}Pb for surface waters at F line are shown in Table 1. The mean residence time of ^{210}Po is calculated by the equation as discribed by Shannon et al.(1970). The ^{210}Po residence time in surface mixed layer of 100 m in thickness were about 2 years, this value is longer than in that of 50 m in thickness. The deffernce of the removal rate of ^{210}Po is suggested that scavenging of ^{210}Po was controlled by particles in surface layer.

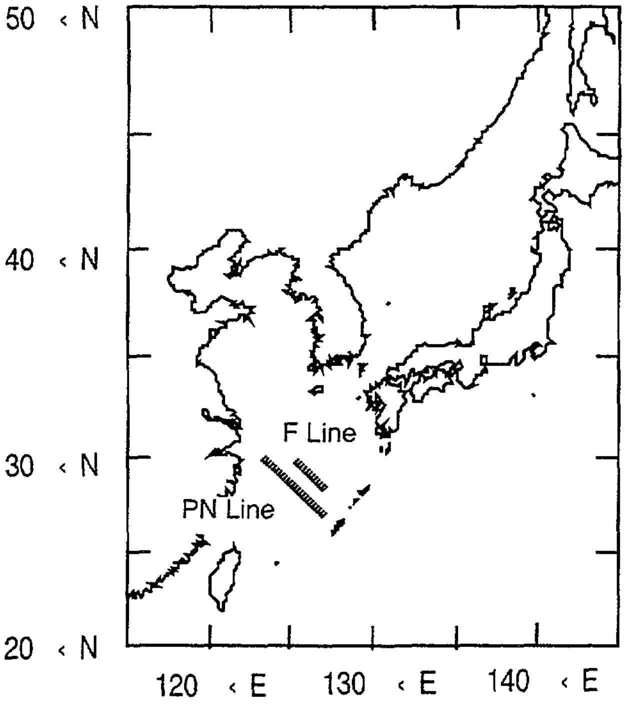

Fig. 1 Sampling locations

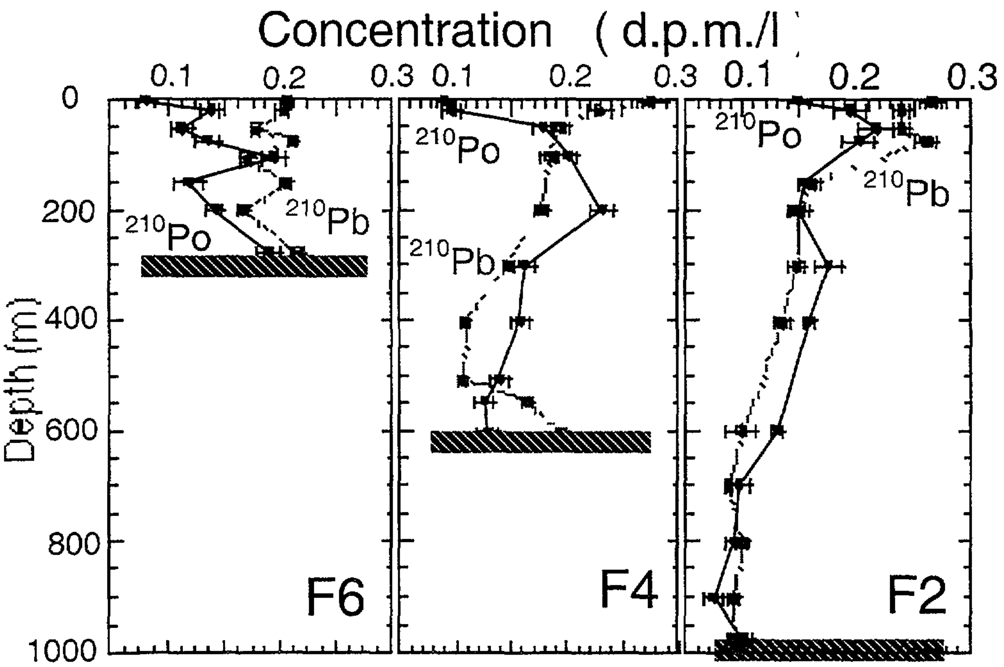

Fig. 2. Vertical profiles of ^{210}Po and ^{210}Pb in the East Sea

Below the subsurface, the ^{210}Po enrichments relative to ^{210}Pb occur and extend to a depth of at least 500 m. The inventories of ^{210}Po enrichments relative to ^{210}Pb in the middle layer were greater 4times than 4 times those of surface depletion. Bacon et al.(1980) suggested that a similar phenomenon was observed in the open tropical Atlantic and was attribute to a efficient recycling of ^{210}Po with the upper thermoline a efficient recycling of ^{210}Po with the upper thermoline.

TABLE I. THE INVENTORIES AND THE ACTIVITY RATIO OF Po210 AND Pb210 IN THE SUBSURFACE OF THE SHELF EDGE OF THE EAST CHINA SEA

STN.	Inventory Po210	(dpm/cm2) Pb210	Activity Ration Po210/Pb210	Po residence (year)
F2	1.02 ±0.03	1.30 ± 0.02	0.78 ± 0.03	2.02
F3	0.74 ± 0.03	1.00 ± 0.02	0.74 ± 0.03	1.58
F4	0.61 ± 0.02	1.16 ± 0.02	0.53 ± 0.02	0.61
F5	0.21 ± 0.02	0.34 ± 0.02	0.62 ± 0.07	0.90
F6	0.19 ± 0.01	0.37 ± 0.01	0.51 ± 0.03	0.59

The concentrations of ^{210}Po was almost constant within the shelf of the East China Sea in the winter. The scavenging residence times of ^{210}Po within the shelf area in winter were 5-10 months, and these within the shelf edge area were ranged from 0.3 to 1.2 years in summer and winter. Although the concentrations of ^{210}Pb and ^{210}Po in the East China Sea were changed in the seasons, these reactive nuclides were scavenged from the water column within a short time in the surface of the shelf of East China Sea.

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IAEA-SM-354/67P

RADIUM DISCHARGE DUE TO OIL OFF-SHORE PRODUCTION - CASE STUDY: BACIA DE CAMPOS, BRAZIL

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The actual Brazilian oil production is of 1 million barrels daily. About 70% is produced on the off-shore oil field called Bacia de Campos localized between Campos and Macaé, Estado do Rio de Janeiro, 60 km far from the coast, with more than 30 platforms in operation (Fig. 1).

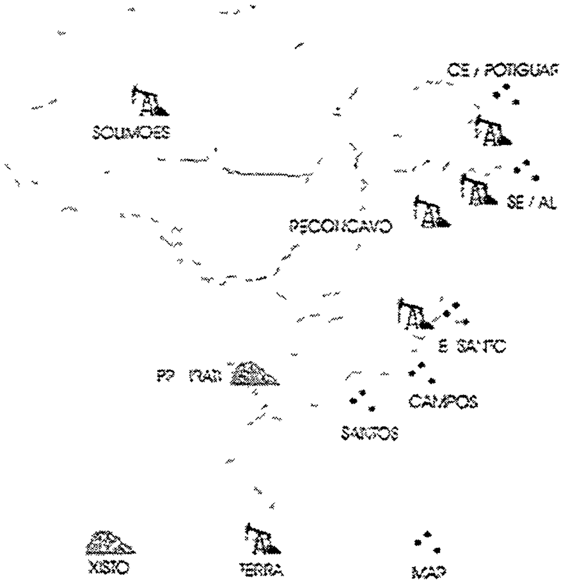

FIG.1. Oil production areas in Brazil.

High levels of ^{226}Ra and ^{228}Ra are present in the formation water around the world. During the oil production, radium is released together with the produced water, or precipitated as radioactive scales on pipelines and separation tanks.

Due to the totally different radiological protection question involved, two research projects have been started at this site. One related with the occupational aspects, and the other with the radium releases to the marine environment. However, it must be clear that both aspects are complementary, since the scale formation reduces the radium releases together with the produced water.

The produced water consists of the mixture of formation water (the water naturally present in the reservoir) with water injected into the formation. Also, in order to maintain the production, sea water may be injected into the formation Therefore, the produced water composition depends upon the relative proportion of formation water versus injected sea water. Since the formation water is rich in barium and strontium and the sea water rich in sulfate and carbonate, the concentration of radium in produced water tends to have the highest values during the first phase of production, when the proportion of sea water is the lowest. On the other hand, later in the life of the off-shore platform, the presence of radium in produced water is reduced, but the scale formation on pipelines and separation tanks becomes an operational problem.

One liter produced water, from several platforms, was taken into glass flasks, and the sample filtered with quantitative grade paper filter. One hundred milliliters diluted with deionised water to one liter. Twenty milligrams of barium added, and barium sulfate precipitated by sulfuric acid addition. The barium sulfate purified as described by [1], including a barium/strontium separation step as barium chromate. Twenty days later, ^{226}Ra and ^{228}Ra were determined based on the alpha and beta counting rate obtained using a low level proportional counter.

Until the present moment, effluent samples from seven different platforms were already analyzed (Table I). The values found are in agreement with the reported in the literature. The platforms number 1 and 2 are the oldest, and, as explained, are those with the lowest radium content in the effluent. It is important to mention that radium concentration in the particulate were equivalent to those found in the dissolved phase.

TABLE I. DISSOLVED ^{226}Ra AND ^{228}Ra CONCENTRATIONS IN THE LIQUID EFFLUENT OF OIL OFF-SHORE PLATFORMS OF BACIA DE CAMPOS

Platform	Period	Ra-226 (Bq L^{-1})	Ra-228 (Bq L^{-1})
Number 1	May/97	0,016	<0,05
Number 3	June/97	2,3	1,6
Number 4	June/97	2,5	12
Number 4	Sept/97	6,0	8,2
Number 1	Oct/97	0,059	0,19
Number 2	Oct/97	0,076	0,10
Number 5	Oct/97	3,7	8,1
Number 6	Oct/97	2,7	1,2
Number 7	Oct/97	0,088	0,35
Number 3	Mar/98	2,0	0,73
Number 3	Mar/98	2,4	4,3
Number 3	Abr/98	4,8	4,7
Number 3	June/98	3,9	<1,4
Number 3	Aug/98	1,6	2,3
Number 1	Aug/98	0,012	0,049
Number 7	Aug/98	0,18	<0,28

Acknowledgements

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PRELIMINARY RESULTS ON LABORATORY SIMULATIONS OF THE DECOMPOSITION OF THE GREEN ALGAE *ULVA RIGIDA*

XA9951982

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The *Ulva Rigida* is a cosmopolitan green algae characteristic of many eutrophic and mesotrophic coastal environments. The effect of its growth and decomposition on the cycle of trace metals has been studied by [1,2] using enclosures in the site Loutropyrgos over a number of years.

The present study is a continuation of that research. Its main aim was to simulate a number of the field experiments in the laboratory, under more controlled conditions and understand better the impact of the decomposition of algae on sea water and sediment.

Three metals were studied in more detail : Cd, Cu and Zn. Fresh sample of algae collected from Loutropyrgos - a site in the Gulf of Elefsis, approximately 30 Km west of Athens - was placed in specially designed tanks under controlled light conditions in sea water collected frequently from the same site, spiked with metals and renewed daily. After the enrichment period of approximately one month, during which algae tissues and water were regularly analysed for trace metals, the algae were cleaned in clean sea water for few days. Then they were left under controlled conditions to decompose and release metal into the water and sediment phases. Betonite of known low metal content, washed and equilibrated for three days in clean sea water of the area was used as the "model" sediment phase. Temperature, dissolved oxygen and pH were monitored in the experimental tank throughout the period of the decomposition of the algae. Cadmium, Copper and Zinc concentrations were determined in sea water, suspended matter, sediment and algal tissues. Further description of the experimental conditions and the relevant results will be given elsewhere.

Perhaps the most impressive of the results reported here is the very high percentage of the particulate metal deriving from the decomposition of the algae. This metal is rapidly removed and deposited to the sediment. 76,5% of the Cd of the algae ended in the sediment whereas 23,5% of it remained in the water column. The relevant percentages for Cu and Zn are 98,5% and 99,3% respectively, ending to the sediment and only 1,5% and 0,7% remaining in the solution. The higher tendency of Cd vs Zn to remain in the diluted phase, has been demonstrated by [3], under the same environmental conditions in speciation studies in the Gulf of Elefsis.

This demonstrates the significance of marine biota and more specifically of massively growing algae in mesotrophic and eutrophic environments for the "trapping", transformation and release of metal species in the relatively narrow and shallow coastal zones where they grow and/or are accumulated.

A second question this study has tried to answer was the assessment of the real impact of the mechanism studied to the natural environment of the site from where the algae were taken, namely Loutropyrgos. For the purpose of the assessment a simple model was developed taking into account the actual growth patterns and the *Ulva rigida* biomass of the study area. The assumption made was that the metal contained in *Ulva rigida* in natural conditions (therefore of lower metal content) will have, after decomposition, the same fate and partitioning as the one in the laboratory experiment. The results are summarised in Table I.

TABLE I. Cd, Cu AND Zn CONCENTRATIONS IN SEA WATER AND SEDIMENT, BEFORE AND AFTER THE DECOMPOSITION OF THE GREEN ALGAE ACCORDING TO THE MODEL FOR THE MARINE AREA OF LOUTROPYRGOS.

	Sea water before the decomposition	Sea water after the decomposition
Cd (μg/lt)	0,3	0,8
Cu (μg/lt)	3,2	3,4
Zn (μg/lt)	11,8	12,3
	sediment	
	before the decomposition	after the decomposition
Cd (μg/g)	4,5	4,6
Cu (μg/g)	23,1	23,5
Zn (μg/g)	112,9	114,3

What one could see is, in our point of view, very interesting. One could observe that the massive growth of algae has a rather small, yet measurable, effect on the natural speciation and the removal trends of the metals studied, affecting to a rather limited extent the conditions of the immediate environment where they grow.

This effect is more obvious for Cd in the dissolved phase, in the water column and for Zn in the particulate phase, in the sediment.

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THE BEHAVIOUR OF ^{99}Tc IN UK WATERS, 1995-1996

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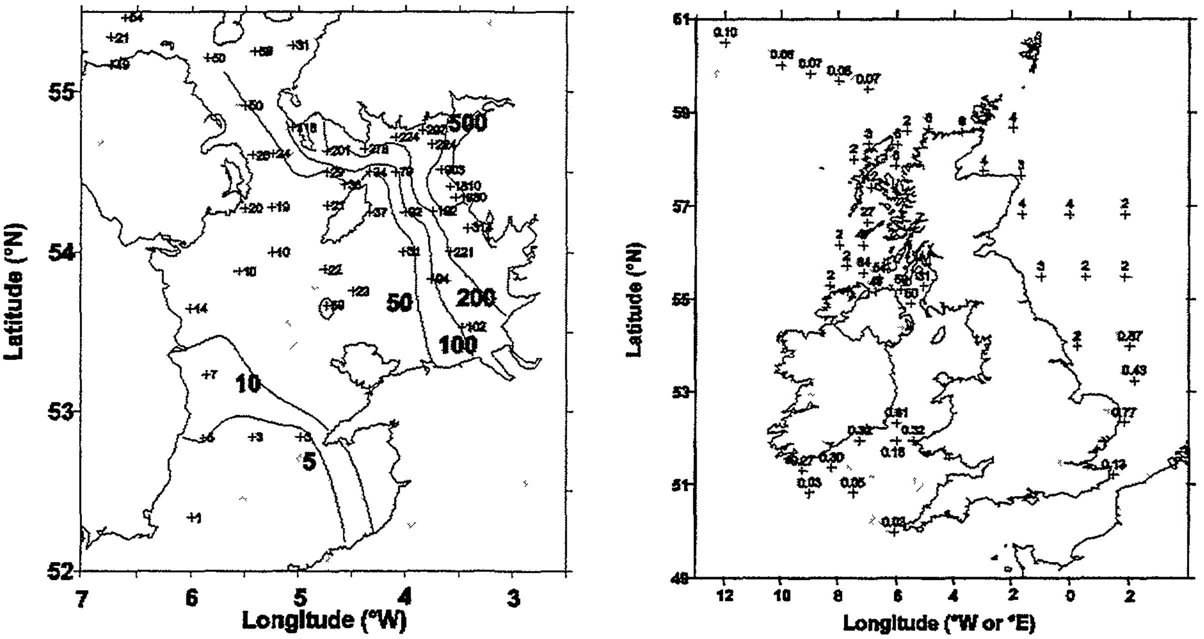
During 1994, in comparison to the releases over the previous decade, the authorised discharges of ^{99}Tc into the northeast Irish Sea from the nuclear reprocessing plant at Sellafield were significantly elevated. The increase in discharges resulted from the additional reprocessing operations of the Enhanced Actinide Removal Plant (EARP). This treatment plant was commissioned to reduce alpha and beta activity from effluents prior to discharge. The initial discharges in 1994 consisted of essentially two distinct ^{99}Tc pulses and provided an unique opportunity to study the migration behaviour of conservative radionuclides in UK waters [1]. A study, carried out following the initial release indicated that the most rapid migration of ^{99}Tc from the outfall to the North Channel was less than 3 months and the mean transit time was estimated to be in the order of 6 months [2]. Furthermore, comparison of UK coastal surveys, prior to and post EARP, suggest that the leading edge of the first ^{99}Tc pulse had migrated to the northern North Sea within some 9 months.

During 1995 and 1996 the pattern of ^{99}Tc discharges changed in that, although the releases remained elevated, the montly discharges were relatively constant. Recent surveys of the Irish Sea and UK waters were carried out in May 1995, December 1995 and December 1996.



A

B

FIG. 1. Distribution of ^{99}Tc (mBq/l) in surface seawater: in December 1995 (A) Irish Sea (B) UK waters.

Using the recent survey data, from 1995 and 1996, information is available of the longer term dispersion behaviour of ^{99}Tc seawater from a continued discharge period. The contour map of ^{99}Tc distribution in the north Irish Sea (Fig 1a) shows that in comparison to previous surveys [2] levels were increased over the entire Irish Sea. Although migration occurs predominantly to the north, the impact of the discharges was also significant in the southern Irish Sea. Further afield, it is apparent that the initial plume from 1994 becomes elongated around the north of Scotland and into the North Sea (Fig 1b). With data for 1996, it is clearly apparent that a slower dispersion has occurred via the western Irish Sea and southwards. In 1996, ^{99}Tc levels in the North Sea have increased by ≈ 50 fold compared with Pre-EARP concentrations.

Although the ^{99}Tc inventories increased following elevated releases in 1994, the majority of discharged ^{99}Tc has been dispersed through the North Channel. In 1995, approximately 84% and 71% of the discharge was transported out of the northern Irish Sea and entire Irish Sea, respectively, over the 12 month period (Table I). During the following year, the values obtained for 1996 were 79% and 54%, respectively. This suggests that increasing seawater concentrations have increased from the cumulative effect of continuous discharges.

TABLE I. ESTIMATE OF ^{99}Tc INVENTORIES (TBq) IN THE IRISH SEA

Cruise	Inventory in northern Irish Sea * (TBq)	Inventory in entire Irish Sea # (TBq)	Year	Annual Discharge (TBq)
12/92	3.5	6.1	1992	3.2
11/93	4.8	7.1	1993	6.1
6/94	29.0	34.4		
12/94	30.5	37.9	1994	72.0
10/95	61.8	93.8	1995	192.1
11/96	95.3	165.5	1996	154.0

* refers to area from 54.0°N- 55.1°N and 2.5°W-6.5°W.
# refers to area from 52.2°N- 55.1°N and 2.5°W-6.5°W.

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ORIGIN AND BEHAVIOUR OF RADIOCAESIUM, PLUTONIUM AND AMERICIUM IN THE SEDIMENT-WATER-BIOTA SYSTEM OF STRANGFORD LOUGH

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Strangford Lough, located on the NE coast of Ireland (Fig. 1), is a marine nature reserve of considerable ecological importance. It has an area of 16.5 kha and is connected to the Irish Sea by narrows through which tides surge and swirl at up to 8 knots. Away from the central channel, much of the lough's seabed is covered by fine silt and mud and, as such, is a potential sink for particle-reactive radionuclides introduced via the Irish Sea following radioactive waste discharges from Sellafield.

Here, we report selected features from a recent (September 1997) detailed study of the radioecological status of the lough, including the spatial distribution of radionuclides in sea water, sediment and biota within the lough, the chemical speciation of Pu in lough waters and measured Pu concentrations through the narrows at ebb and flood tide.

Our data (Fig. 1) show that radionuclide levels within the lough are similar to (or lower than) those in the adjacent NW Irish Sea and that most of the activity is of Sellafield origin. In general, ^{137}Cs, ^{239,240}Pu and ^{241}Am levels diminish with increasing distance from the narrows, more than

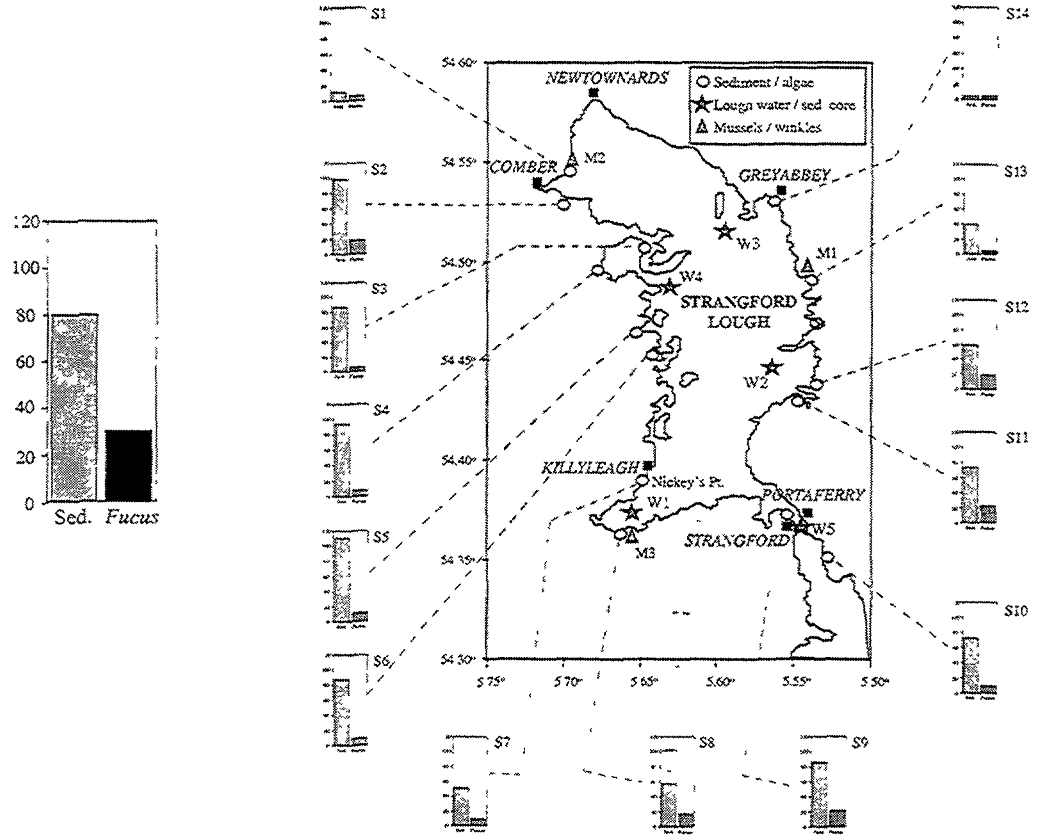

FIG. 1. Sampling sites throughout Strangford Lough. ^{137}Cs concentrations (Bq kg^{-1}, dry wt.) in intertidal sediment and brown algae (Fucus vesiculosus) are also shown.

likely due to scavenging by particulate matter, as the salinity gradient is very weak (32–34‰). We did not detect any (significant) difference in the input and output fluxes of Pu through the narrows at flood and ebb tide (Table I). This is not unexpected as, on a volume basis, the water within the lough as a whole is exchanged with NW Irish Sea water about once every four tides.

Examination of published time-series data (Fig. 2) show that ^{137}Cs and Pu concentration trends in sediment and algae within the lough have closely followed those in the NW Irish Sea, in that while ^{137}Cs concentrations have fallen steadily over the past decade or so, Pu concentrations have remained virtually unchanged.

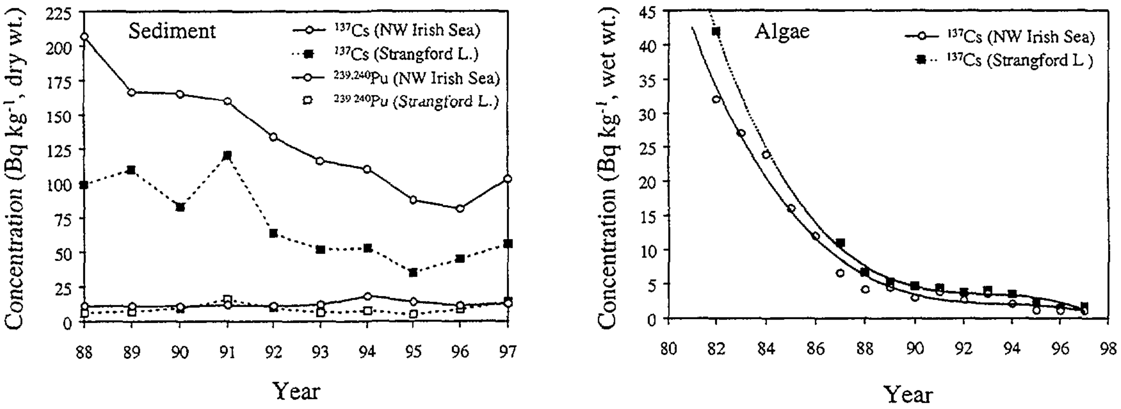

FIG. 2. ^{137}Cs and Pu levels in marine materials from Strangford Lough and the NW Irish Sea.

Our analyses show that the physico-chemical speciation of Pu in the lough is similar to that in the NW Irish Sea (Table 1), once allowance is made for the considerably higher particulate loading in lough waters. Total Pu concentrations in lough waters are at least an order of magnitude higher than those observed in open ocean waters affected solely by global fallout and confirm that Sellafield-sourced effluent has penetrated lough waters. Measurement of the ^{238}Pu/^{239,240}Pu activity ratio (0.20 ± 0.02; n=10) provides unambiguous evidence of the latter and shows that at least 95% of the current Pu inventory in the water column is attributable to Sellafield. A similar observation applies to Pu and Am in lough sediment.

TABLE I. PHYSICO-CHEMICAL SPECIATION OF Pu IN STRANGFORD LOUGH WATERS

Station	**Fraction**	**Concentration(mBq m^{-3})**		**^{238}Pu/**
		^{238}Pu	**^{239,240}Pu**	**^{239,240}Pu**
Stn. W1	Filtered	50 ± 3	257 ± 11	0.195 ± 0.014
	Particulate	21 ± 2	132 ± 6	0.161 ± 0.017
	Total	71 ± 4	389 ± 13	0.183 ± 0.023
Stn. W2	Filtered	53 ± 3	277 ± 8	0.190 ± 0.011
	Particulate	19 ± 2	82 ± 4	0.23 ± 0.03
	Total	72 ± 3	359 ± 9	0.200 ± 0.010
Stn. W3	Filtered	38 ± 2	167 ± 7	0.225 ± 0.017
	Particulate	4.5 ± 0.9	22 ± 2	0.21 ± 0.04
	Total	43 ± 2	189 ± 7	0.228 ± 0.014
Stn. W4	Filtered	17.9 ± 1.1	98 ± 3	0.182 ± 0.012
	Particulate	10.4 ± 1.7	43 ± 4	0.24 ± 0.05
	Total	28 ± 2	141 ± 5	0.199 ± 0.016
Stn. W5 (flood)	Total	79 ± 3	434 ± 11	0.182 ± 0.007
Stn. W5 (ebb)	Total	89 ± 3	450 ± 9	*0.198 ± 0.007*
Mean (n = 10)				*0.20 ± 0.02*

Station	**% particulate**
Stn. W1	33.9 ± 1.3
Stn. W2	22.9 ± 1.0
Stn. W3	11.6 ± 1.0
Stn. W4	30 ± 2
Mean (n = 4)	*25 ± 10*

Location	**%Pu(V,VI) in filtrate**
Stn. W1	87 ± 1
Stn. W3	85 ± 1
Mean	*86 ± 1*
NW Irish Sea	85 ± 5 (n=9)

In radioecological terms, Strangford Lough behaves as an extension of the NW Irish Sea. The turn-over rate for waters within the lough is sufficiently rapid to ensure that both dissolved and particle-reactive radionuclide levels mirror those prevailing in the NW Irish Sea.

EFFET DE LA POLLUTION SUR LA COMPOSITION SPÉCIFIQUE ET L'ABONDANCE DU ZOOPLANCTON DANS LES EAUX CÔTIÈRES SYRIENNES

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La comparaison de la composition spécifique du zooplancton, des eaux relativement polluées avec d'autres considérées propres, fait l'objet de ce premier genre du travail dans les eaux côtières syriennes.Une différence nette a été enregistrée en nombre d'espèces déterminées et dans la composition spécifique pour les deux types d'eaux.

Notre étude est basée sur 142 échantillons, pris lors de 36 sorties en mer. Elle a été réalisée en deux régions : La première est en face de Lattaquié (mars - octobre 1991 et avril-octobre 1992); la deuxième est en face de Banyas (juin 1995-juin 1996), avec une sortie par mois en moyenne. Les échantillons ont été collectés en surface (-0,5m) à l'aide d'un filet de type WP2 (200 µm de vide de maille, 176 cm. de diamètre et 56 cm. de diamètre d'ouverture) et avec une durée de pêche de 5 minutes. Dix stations à caractéristiques écologiques différentes ont été retenues: quatre d'entre elles se situent dans la région de Lattaquié et six autres dans la région de Banyas; ces stations ont été réparties entre stations de références et stations sujettes à différentes types de pollution (urbains, pétrolier et thérmique). les mesures hydrologiques concernant la salinité et la température ont été effectuées simultanément avec les pêches et celles chimiques (sels nutritifs) ont été réalisées plus tard au laboratoire. La détermination du zooplancton est faite jusqu'à l'espèce et le comptage des individus de chaque espèce est réalisé dans des sous-échantillons. L'abondance (ind./m3) des différentes espèces a été calculée en divisant le nombre d' individus dans l'échantillion sur le volume d'eau filtré par le filet (calculée à son tour, à partir de la longueur du trajet parcouru par le bateau et l'ouverture du filet)

Plus de 170 espèces zooplanctoniques ont été détérminées dont 78 copépodes, soit 51% de la diversité du zooplancton, dans la région de Lattaquié [1]. Le nombre d'espèces a été, remarquablement, plus élévé dans la région de Banyas avec 300 espèces dont 119 copépodes (36.6% de la diversité totale). Tous les groupes zooplanctoniques méditerranéens ont été présents dans les eaux étudiées. Il paraît que la pollution agit, d'une façon ou d'une autre sur la composition spécifique du zooplancton; le nombre total d'espèces définies, dans la région de Lattaquié, a oscillé entre 71-89 aux stations polluées et 115 espèces dans la station de référence. La différence entre les stations de Banyas a été plus modérée où ce nombre a varié entre 124 et 166 espèces; la limite supérieure a été enregistrée dans des station relativement propres. Du même, l'indice de diversité (I=S-1/logN, S: nombre d'espèces et N: abondance/m3) a montré aussi certaine variation suivant la nature écologique des stations étudiées (Moyen = 3.94-4.7 bits.ind. à Lattaquié, et 5.25-7.66 bits.ind. à Banyas); les fortes valeures dans la région de Banyas, sont dues à la faible abondance du zooplancton dans cette région où l'abonance maximale n'a pas depassé 3100 ind./m3 contre plus de 10000 ind./m3 dans la région de Lattaquié. Par ailleurs, les valeures maximales de l'abonance se sont engistrées dans des stations riches en sels nutritifs azotés (ayant les effluents urbains comme origine principale).

Les copépodes ont formé, souvent, plus de 80% de l'abondance totale du zooplancton.La majorité d'espèces sont communes à toutes les stations dans chaques région; mais, des espèces spécifiques ont caractérisé chacune de dix stations. Les espèces du genre Acartia et surout *A. grani* et *A. discaudata* sont, presque, limitées aux stations polluées en hydrocarbures; cela a été constaté par plusieurs chercheurs [2].Les larves des crustacés ont, aussi, marqué leur diversité et leur abondance maximale dans des stations polluées par les rejets urbains.

TABLEAU I. VALEURS DES PRINCIPAUX PARAMÈTRES ÉTUDIÉS

Paramètres	Région de Lattaquié	Région de Banyas
Témperature	15-32	16.6-36
Salinité ‰	24-40.4	33.3-40.6
NO_3 (ug/l)	nd-17	0.8-27.2
NO_2 (ug/l)	nd-0.7	0.02-0.63
NH_4 (ug/l)	nd-4.5	0.009-3.5
PO_4 (ug/l)	nd-1.4	0.02-14
Nb.d'espèce	71-115	124-166
Ind.diversité (bits.ind.)	3.94-4.7	5.25-7.66
Ab.(ind/m^3)	16-10000	10-3100

nd: non détecté

Nous avons calculé le coefficient de corrélation entre le nombre d'espèces détérminées et les différents paramètres hydrochimiques illustrés dans le tableau (1). Une corrélation négative a été trouvé entre le nombre d'espèces et les concentrations de sels nutritifs azotés; le coéfficient de corrélation était de l'ordre de -0.31 pour le nombre d'espèces et les nitrates; cette relation est illustrée par une régression liniaire (Figure 1). La diminution du nombre d'espcèces dans des eaux polluées en comparaison avec d'autres propres en voisinage a été également remarqué par [3] et [4].

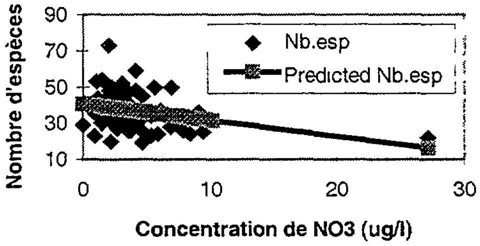

FIG.1. Rrelation entre le nombre d'espèces et la concentration de nitrate dans la région de Banyas. y= 40.50- 0.885(x)

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XA9951986

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THE FATE OF NUTRIENTS AND PHOSPHATES IN AKROTIRI BAY, CYPRUS BASIN (EASTERN MEDITERRANEAN LEVANTINE BASIN)

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The pathways and the levels of the concentrations of nutrients resulting from the discharge of treated effluents from the Limassol Sewage Treatment Plant (SALA) and from marine fish farms in Akrotiri Bay were studied through numerical simulations of the dispersion of phosphates and nitrates. The use of a dispersion model made it possible to evaluate different courses of action regarding both, the protection of the marine ecosystem and the development of marine fish farm activities. Akrotiri Bay is a semi-open coastal sea area in the Eastern Mediterranean Levantine Basin bounded to the North and West from the south coastline of Cyprus. Nutrients inputs from the discharges of SALA result in the elevation of the background levels of nutrients and in particular those of phosphates.

The flow in the Cyprus Basin and wind forces are capable of influencing the circulation in Akrotiri Bay. The northern periphery of the mid-Mediterranean jet and the western extension of the Cyprus Basin Cyclonic Eddy contribute to the formation of a local eastward flow in spring and autumn (1996) [1]. The Lagrangian current meter measurements in the coastal zone of interest confirm a marked seasonal flow variability, eastward during winter and spring and westward during summer and autumn [2].

In order to investigate the possible long distance transport and the dispersion of nutrients in Akrotiri Bay, 2D and 3D flow and dispersion models [3] for conservative pollutants in a homogeneous water column was applied (the upper mixed layer reaches down to 30-40 m depth-much deeper than the depth where most of the fish farm units are located). In accordance with the dominant wind field, the westerly and easterly sector winds are used to force the flow model. The westerly sector winds generate in the bay an eastward current flowing along the coastline and a small scale cyclonic vortex near the western coastline. A reversal of the currents was simulated in the case of easterly sector winds. Both cases are in agreement with the observed current measurement [4].

Several numerical experiments have been performed to simulate the pathways of conservative pollutants for nitrate and phosphate loads from SALA and those due to existing and planned marine fish farms in the bay. The dispersion models used to simulate the conservative pollutant concentrations. Nitrates are utilized by phytoplankton which extrudes part of the assimilated nitrogen because of respiration and mortality rate, creating detritus, which is remineralized in nitrates. The aggregated formulation is conservative under the simplifying hypothesis that the non conservative processes of the nitrogen cycle are in dynamic balance [5]. The existing nutrient loading of the marine environment in Akrotiri Bay is 22 tonnes of Nitrogen and 4.4 tonnes of Phosphorous per year. The model simulations for dissolved nitrogen and phosphorous indicate that the SALA sea outfall and the marine aquaculture production increase these nutrients by 0.14 mmolN M-3 and 0.04 mmolP M-3. The present nutrient loading in the area, based on in-situ measurements, results in 100% and 15-30% increases of the winter background levels of phosphate, at a distance of 4 and 10 km from the SALA outfall respectively [6]. The % increase of phosphate concentrations during spring and summer periods are much higher as the background levels are practically zero.

Westward simulated dispersion of phosphates in Akrotiri Bay from existing sources

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STUDIES ON PLUTONIUM AND AMERICIUM IN COASTAL ENVIRONMENT OF BOMBAY HARBOUR BAY

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Low level treated radioactive effluents generated at the Bhabha Atomic Research Centre are discharged at CIRUS situated on Trombay shore. The discharges are made at 825m away from the shore where 1.8m depth of water is available even at neap tide.

Bombay Harbour Bay (Latitude 18^0 51' to 19^0 10' N Longitude 72^0 48' to 73^0 00' E) is a land locked mass of water which opens into the Arabian sea. The bay narrows down to the Thane creek in the north and receives water from Ulhas river and Pen river on the land locked portion and Amba river at the south where bay joins the Arabian sea. Fish and salt are the main significant commodities produced from the bay.

Studies on the distribution and accumulation of $^{239+240}$Pu and ^{241}Am in different matrices of the bay environment are necessary to assess the impact of released radioactive effluents on the environment. Regular monitoring of the aquatic environment of bay is carried out by analysis of samples like sea water, sediment (shore and bottom), marine organisms and salt. The paper presents the study for the period of two decades and arrived on Kd's in sedments , Bp values in organisms, temporal and spatial variation of these radionuclides in the bay and internal dose calculation to the member of public and critical group of population.

The methods used for processing the samples and the sequential method adopted for estimating plutonium and americium are reported elsewhere [1,2]. Analytical quality is checked by participating in inter-laboratory intercomparison exercise in collaboration with IAEA [2,3,4].

Concentration of $^{239+240}$Pu and ^{241}Am for sea water, coastal and bottom sediments, pelagic and benthic organisms and solar salt are indicated as a range of concentrations for the period 1977-1995. Sea waters ($^{239+240}$ Pu: 0.03 -2.6 mBq.l^{-1}, ^{241}Am: <0.006- 0.9 mBq.l^{-1}) , coastal and bottom sediments ($^{239+240}$Pu: 0.028-8.38 Bq kg^{-1},^{241}Am: <0.01-3.1 Bq kg^{-1}) showed slightly elevated concentration of the radionuclides around the discharge area (0-3km). Values across the other shore at 6 km and at the mouth of the Bay at 20 km from discharged area are at fallout levels(5) (Sea water: $^{239+240}$ Pu:0.01-0.033 mBq l^{-1}, ^{241}Am: <0.006 mBq l^{-1} and Sediments: $^{239+240}$Pu:0.038 -0.098 Bq kg^{-1}, ^{241Am}:<0.01 Bq kg^{-1}).

Temporal variation in the concentration of $^{239+240}$Pu in sea water and the sediments of the bay for the years between 1988 to 1994 is negligible. There is a very small but steady increase in ^{241}Am concentration in sea water with time. Temporal variation of the concentration of ^{241}Am in sediments is negligible. Studies on seasonal variation in sediments between pre and post- monsoon for $^{239+240}$Pu concentration did not show any perceptible change due to monsoon. The spatial variation along the Trombay shore of the Bay indicates a decrease of plutonium and americium concentration on either side (i.e., north and south) at 3 to 11km of the discharge area by a factor of 2 to10. However, there is a net northerly transport of $^{239+240}$Pu and ^{241}Am from the discharge area through sea water and sediments.

$^{239-240}$Pu and ^{241}Am values in salts ($^{239+240}$ Pu:< 0.08 to 6.2 mBq Kg^{-1} dry, ^{241}Am: <0.08-0.48 MBq kg^{-1} dry). These values in literature are scanty and hence assume significance. However, there is no preferential accumulation of these radionuclides in salt.

The values in pelagic fish $^{239+240}$ Pu:0.21-33.03 MBq kg^{-1} wet, ^{241}Am: <0.6 - 16.83 MBq kg^{-1} wet) and for benthic crustaceans ($^{239+240}$ Pu:0.01-2.59-640 MBq kg^{-1}wet, ^{241}Am: 0.83-65 MBq kg^{-1} wet).

Distribution Coefficient, Kd, values for the sediments for $^{239+240}$Pu and ^{241}Am obtained are 1.06×10^{5} and 1.0×10^{6} respectively [3,4]. These are comparable with IAEA's values [6] Bioaccumulation Factor, Bp, values for the pelagic fish and benthic crustaceans obtained are 140 and 670 respectively for $^{239+240}$ Pu and 180 and 1050 respectively for ^{241}Am [3, 4]. The Bp values for benthics are higher by a factor of 2 to 5 compared to the values for IAEA [6].

Applying the latest dose conversion factors for plutonium and amerisium given by ICRP [7], the total internal dose to the critical population of fishermen and to a member of the public due to $^{239+240}$Pu and ^{241}Am through ingestion of fish and salt works out to 0.57μSv y^{-1} and 0.155 μSv y^{-1} respectively, compared to the prescribed limit of 1000 μSv y^{-1} [8]. Thus, the values are lower by a factor of 1750 for critical population and by 6450 for a member of the public.

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IAEA-SM-354/78P

THE IAEA '97 PACIFIC OCEAN EXPEDITION

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IAEA(1)-German(2)-Indian(3)-Japanese(4)-Korean(5)-Swedish(6) Collaboration

The International Atomic Energy Agency's Marine Environment Laboratory (IAEA-MEL) started in 1995 a five-year project "Research on World-wide Marine Radioactivity", generously supported by the Government of Japan. In the framework of the project, IAEA-MEL conducted the "IAEA '97 Pacific Ocean Expedition" to the NW Pacific Ocean from 21 October to 20 November, 1997. The objectives of the expedition were to provide new data on the current marine radioactivity in order to compare them with data sets obtained during national and international surveys at sites used for radioactive waste dumping or nuclear bomb testing in the NW Pacific Ocean and its marginal seas.

The expedition was organized in cooperation with Federal Maritime and Hydrographic Agency (BSH), Hamburg (Germany), Korea Ocean Research and Development Institute (KORDI), Seoul (Republic of Korea), Physical Research Laboratory (PRL), Ahmedabad (India), University of Linköping (Sweden) and five Japanese institutes : Japan Atomic Energy Research Institute - Mutsu Establishment (JAERI-Mutsu), Japan Chemical Analysis Center (JCAC), Japan Marine Science Foundation - Mutsu Marine Laboratory (JMSF-MML), Meteorological Research Institute (MRI) and Tokai University. Twenty two participants from the five Member States, including six staff members from IAEA-MEL, took part in the expedition.

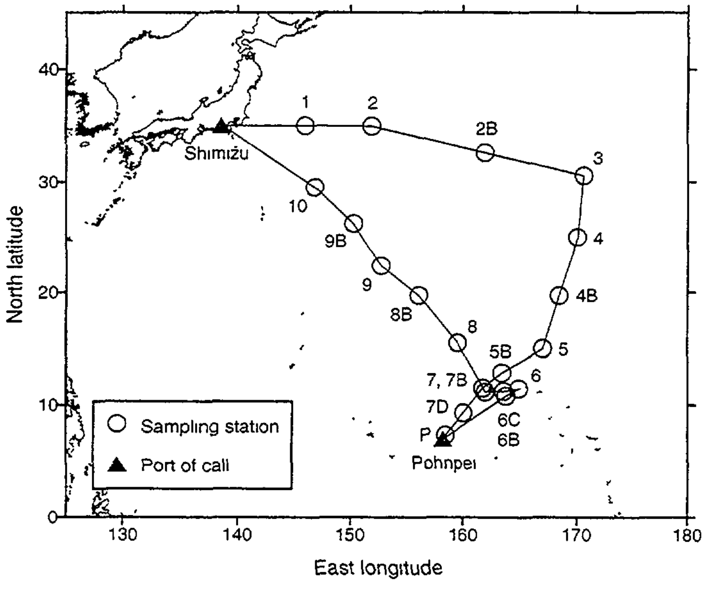

FIG.1 The route and sampling stations for the IAEA '97 Pacific Ocean Expedition.

The expedition was conducted using a research vessel 'Bosei Maru' owned by Tokai University. **Fig.1** shows the route and sampling stations for the expedition. The route was in a triangular shape from Shimizu (Japan) eastward to Milwaukee Sea-Mountain (St. 3), then southward to the Marshall Islands (St. 6 and 7), calling at Pohnpei (The Federated States of Micronesia) and back to Shimizu. The sampling work in the NW Pacific Ocean was carried out at 20 stations, including 4 GEOSECS stations [1] (St. 2, 2B, 3 and 4) and 7 stations close to the Bikini and Enewetak Atolls (St. 5B, 6, 6B, 6C, 7, 7B and 7D).

Seawater samples were collected at several layers using large volume water samplers (LVS), submersible pumps and a CTD system with rosette multi-bottle samplers (CTD/RMS). Sediment and biota were sampled by a box corer and fishing rods/nets, respectively. CTD and general chemistry measurements were also carried out during the expedition. **Table 1** gives samples collected and measurements performed at each sampling station. In total the following samples were collected : 5 sets of large volume water samples with 7-10 depths, surface water samples at all the 20 stations, 12 sets of small volume water samples with 6-18 depths, 15 cores of sediment samples at 4 stations with 23-36 cm in length, 45 fish samples at 6 stations with 3 different species and plankton samples at 3 stations. Pre-concentration chemistry was carried out on board to reduce the volume of large volume water samples by a factor of about 20, so that the samples could be sent by surface freight from Shimizu to Monaco and to laboratories of the participating Member States.

TABLE I. SAMPLES COLLECTED AND MEASUREMENTS CARRIED OUT DURING THE IAEA '97 PACIFIC OCEAN EXPEDITION
(* C : CTD/RMS, L : LVS, W : SURFACE WATER, S : SEDIMENT, B : BIOTA)

Station	Date	Depth (m)	Sample*	Station	Date	Depth (m)	Sample*
1	23-25/Oct	5920	C, L, S	P	6/Nov	4240	C, W
2	26/Oct	6100	C, W	6B	9/Nov	-	W
2B	28/Oct	5920	C, W, B	6	9-11/Nov	4530	C, L, S, B
3	29-30/Oct	5470	C, L, B	6C	11/Nov	-	W
4	31/Oct-1/Nov	5970	C, W	7B	11-12/Nov	3690	L
4B	2/Nov	-	W, B	8	13-14/Nov	5490	C, L, S
5	3/Nov	4860	C, W	8B	15/Nov	-	W
5B	4/Nov	-	W	9	16/Nov	5600	C, W, S, B
7	4-5/Nov	3500	C, W, B	9B	17/Nov	-	W
7D	5/Nov	-	W	10	18/Nov	6000	C, W

Preliminary results obtained by CTD and general chemistry measurements performed during the expedition are presented in a cruise report issued soon after the expedition by IAEA [2]. The full analyses of collected samples will be carried out by IAEA-MEL and Member States' laboratories including those of the participating organizations. The final results of all the analytical work will be published elsewhere.

In spite of the difficult weather conditions during the first half of the expedition (five typhoons crossed the sampling stations), the scientific objectives of the expedition were fulfilled thanks to the hard work and extra efforts of all participants and the ship's crew. It was the first time in the history of the IAEA that an oceanographic expedition to the open ocean was fully organized and accomplished by the Agency.

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IAEA-SM-354/79P

CAPRELLA WATCH; A NEW APPROACH FOR MONITORING BUTYLTIN RESIDUES IN THE OCEAN

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The use of butyltins (BTs) in the marine environment has been found of great concern due to the leterious effects on a wide range of aquatic organisms. Although Japan as well as in other developed untries in the early 1990s placed restrictions on the usage of tributyltin (TBT) as an antifouling agent for astal boats and aquaculture beds, levels of BTs in the marine environment remain at high.

Recently, we have conducted a comparative study on the levels of BTs in seawater and in various ganisms in the marine ecosystem of Otsuchi Bay, northern Japan. The results show that relatively high ncentrations of BTs occur in Caprella spp., one of the dominant secondary producers, inhabiting the algal mmunities and aquaculture beds, while concentrations in seawater were less than the detection limit [7]. ιprella spp. are small amphipod crustaceans with the following characteristics;

1) Well-adapted morphology for clinging to substrata such as algae and hydroids with reduced appendages which are used for swimming in other amphipods [8].
2) Lack of planktonic larval stages.
3) A shortened generation length of ca. 1 to 3 months [9, 10].
4) A high biomass in algal communities [11].

Assessments of the levels of BTs and their toxic effects on the marine ecosystem, studies have ncentrated in several group of animals, e.g., marine mammals [1, 2], small tuna species [3], squids [4], ogastropod snails [5] , and mussels [6]. Of these key-stone animals, the former three groups inhabit off-ore and oceanic areas and have an ability to migrate over long distances, suggesting their levels of BTs ;idues reflect on a global scale . Contrary to these larger animals, the latter two invertebrate groups as :ll as Caprella sp. inhabiting intertidal to the upper part of subtidal zone reflect the BTs residues mainly in allow coastal ecosystems.

The characteristics of caprellids indicate that the concentrations of BTs in Caprella spp. reflect the tyltin residues in the water at the collecting site during the previous few months. Especially, the short ε span of less than a year is useful for monitoring the bioavailability of BTs residues over the short time ıle (Fig. 1), since the life span of neogastropod snails and mussels are usually longer than 2 years and ιched more than 10 years in several cases in the temperate regions [12, 13].

Thus, we propose the establishment of a new monitoring system for the detection of BTs over small atial and temporal distance using Caprella spp. as a "bio-sensor"

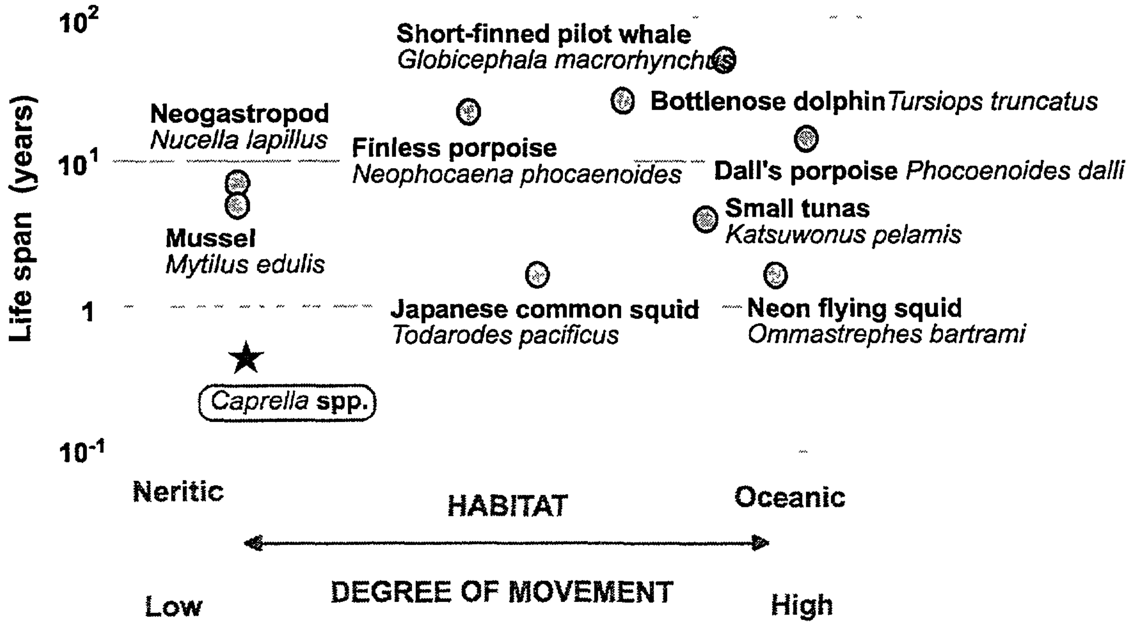

FIG. 1. Schematic view of the life span and habitat of key-stone animals used for monitoring butyltins in the Ocean.

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IAEA-SM-354/81P

ENVIRONMENTAL POLLUTANTS IN THE KARA SEA AND ESTUARIES OF OB AND YENISEY

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The Arctic has been identified as an area that is particularly vulnerable to adverse effects from environmental perturbations. Renewed attention has been focused on examining levels and assessing the effects of anthropogenic pollutants found in critical habitats within the Arctic. In 1993, the Russian-Norwegian oceanographic programme (RusNoP) launched the scientific program KAREX, an investigation in the Kara Sea and the estuaries of the Ob and Yenisey. RusNoP is a co-operation between the Arctic and Antarctic Research Institute and the Norwegian Polar Institute. The primary objective of the KAREX-94 program was to identify current levels of sediment-bound contaminants in the Kara Sea region and to elucidate possible contaminant transport routes. Pollutants measured in seabed sediment samples and an assessment of benthic macrofauna communities are presented in this paper. Pollutants examined are hydrocarbons, organics, pesticides, and heavy metals. Information on radionuclides is presented in this symposium by Carroll et. al. The KAREX-94 program also included analyses performed on suspended matter, ice, and biota. Oceanographic and geochemical data were collected and are being used to investigate mechanisms for incorporation of solid materials into sea ice, transport routes of ice out of the Kara Sea, and deposition of ice-incorporated sediments. The Karex-94 expedition was planned in co-operation with the Arctic Monitoring and Assessment Programme (AMAP) and the data obtained has been made available to the AMAP assessment report [1].

On the Kara Sea Shelf, concentrations of total non-polar petroleum hydrocarbons (THC) measured in samples from shallow areas ranged from less than 1.2 mg/kg (detection limit) to 68 mg/kg. The levels represent mild (<10 mg THC/kg dry weight) to moderate (10-100 mg/kg) contamination in these areas. Polyaromatic hydrocarbon (PAH) concentrations were near background levels at all sampling stations (7-184 μg/kg) except one (265 μg/kg). One other station, near the Kara Gate (334 μg/kg) is classified as moderately contaminated (300-2000 ug/kg). Concentrations of THC (8-164 mg/kg) and PAH (49-590 μg/kg) measured in the Ob and Yenisey estuaries were generally higher than on the shelf. Comparing concentrations within the estuaries, higher PAH levels were detected in samples from the Yenisey. Concentrations of both THC and PAH are slightly higher than were measured in previous expeditions.

Low levels of PCB and pesticides, resembling background levels, were found at most stations both on the Kara shelf and within the estuaries of the Ob and Yenisey. Moderately elevated levels of PCB and some persistent organochlorines as well as markedly elevated levels of DDT were found near the Kara Gate. Moderately elevated levels of DDT were also observed at two stations in the Yenisey estuary.

Heavy metal concentrations (Al,As,Cd,Cr,Co,Cu,Fe,Mn,Ni,Pb,V,Zn,Li,Mo) were measured in surface sediment samples and sediment cores. The data indicate that, except for some anomalous As, Cu, and Ni values, the metal levels on the Kara Sea Shelf and in the Ob and Yenisey estuaries are near or at mean natural background levels of other circumpolar shelf sediments. Metal concentrations were much lower than anticipated from speculative reports of extensive contamination for some Arctic marine areas.

There was a high heterogeneity in species representation and general faunal community structure across the sampling area. On average, the marine stations sampled contained approximately 130 taxa, represented by 1 620 individuals per m^2, while the estuarine stations contained around 27 taxa, represented by 600 individuals for the same sampling area. The biomass at the marine stations was almost 200g per m^2, while the estuarine areas contained only around 26g per m^2. Using canonical correspondence analyses, the only significant environmental variable which explained the faunal variance was mud (particles less than 63μ in diameter). Certain species showed an affinity with the deep stations, while others were associated with shallow areas, although water depth in itself was not a significant variable. It is expected that incorporation of factors related to sedimentation rate and bioturbation will help to clarify the overall picture.

The general conclusions of the Karex-94 program are supportive of findings from similar monitoring investigations conducted for this region. Measured concentrations of most contaminants are quite low. However, as of yet, contaminant fluxes are not well characterized and the potential for ice transport of contaminants is still poorly understood. While benthic macrofauna exhibit high biomass and abundance, environmental controls on community structure are currently uncertain. Future investigations will help to identify existing linkages between environmental contaminants and biological communities. In the context of current projections for industrial development in these Arctic areas and our present knowledge of environmental "hot spots" in the Russian Siberia, new programs are warranted.

Acknowledgment

The KAREX-94 program was supported financially by Norwegian Ministry of Environment. Participating organizations were Norwegian Polar Institute, Akvaplan-niva AS, Agricultural University of Norway, and Norwegian Radiation Protection Authority. Participating Russian organizations were Arctic and Antarctic Research Institute (St. Petersburg), Russian Center for Mapping and Assessments (St. Petersburg) and Moscow University.

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IAEA-SM-354/83P

ENVIRONMENTAL BEHAVIOUR OF PESTICIDES IN RICE FIELD DRAINAGE WATER. IMPACT ON THE COASTAL ZONE.

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Experiments were carried out to assess the behaviour of pesticides in the drainage water from a rice field.

For the first experiment a segment of a rice field drainage channel was chosen whose dimensions were: length 1200 m; average width 2 m; depth 0,3 m. The flow rate at the moment of the experiment was 83 l/min while the linear water velocity was 20 m/min. At a point, chosen as the beginning of the experiment, a pesticide mixture was poured at 6 liter/minute, during 10 minutes. The concentration of each pesticide in that mixture was such that after leaving this point, the flowing water had an initial concentration (mg/l) of: dimethoate 0,6; iprobenfos 0,7; parathion methyl 1,5; malathion 1,4; chlorpyrifos 0,72; cypermethrin 0,05 and endosulfan ($\alpha+\beta$) 1,0.

Exactly ten minutes after the pouring of the pesticide ended, began the water sampling at the first sampling point (200 m. downstream from the starting point). There, water was sampled at a rate of 1 l/min during 10 minutes. After mixing , a 2,5 l sub sample was taken for analysis.

Twenty minutes later began the sampling in the second point (Fig 1). There, water was taken at the same rate and during the same time as in the first point. Other two samples were taken at 1000 m and 1200 m from the starting point in the way already explained:

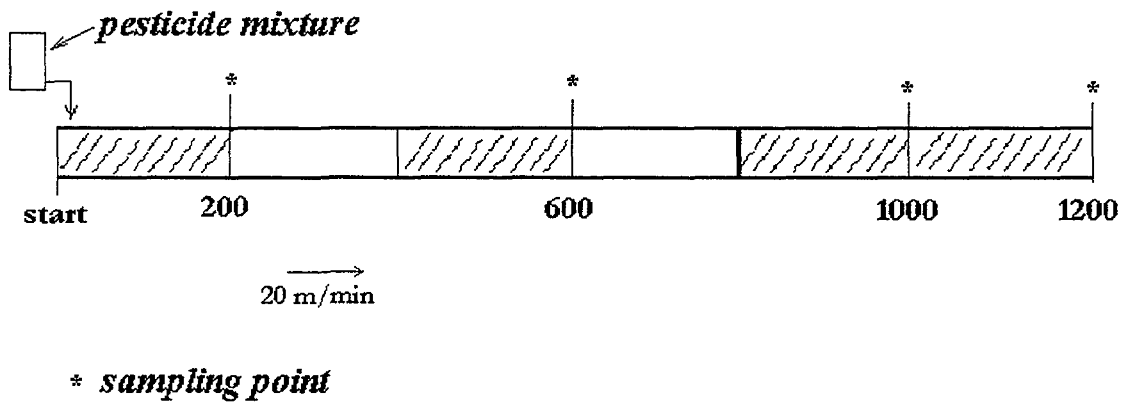

FIG. 1. The sampling in the second point

The second experiment was conducted in the same place. The water flow rate was 2,4 times higher than in the previous experiment. In this case, the initial pesticide concentrations were adjusted to half the values of the first experiment. Carbofuran was included with an initial concentration of 0,35 mg ai/l.

As a general trend, the concentrations of all the pesticides were lower, the longer the distance from the starting point and very low and in some cases not detected at the final sampling point (see table). Also the higher the flow rate, the lower the distribution of the pesticides betwen water and sediment and higher the concentration at the final sampling point.

These results allow the management of the impact of the drainage water on the coastal zone, by slowing down the drainage flow (widening the channels) or simply extending the drainge time. Both measures will effectively reduce the presence of pesticide residue in the waters that mouth on the coastal zone.

TABLE I. DYNAMIC ADSORPTION OF PESTICIDES UNDER FIELD CONDITIONS.

Pesticide	Experiment	Initial conc (mg/l)	Concentration found at the indicated points (mg/l) 200 m	600 m	1000 m	1200 m
Dimethoate	1	0,6	0,40	0,01	ND	ND
	2	0,3	0,01	ND	-	ND
Iprobenfos	1	0,7	0,30	0,006	0,003	0,006
	2	0,35	0,27	0,02	-	0,003
Parathion methyl	1	1,5	0,40	0,009	0,003	0,008
	2	0,75	0,53	0,04	-	0,06
Malathion	1	1,4	0,50	0,008	0,007	0,001
	2	0,7	0,54	0,1	-	0,07
Chlorpyrifos	1	0,72	0,12	0,005	0,004	0,002
	2	0,36	0,11	0,003	-	0,001
Cypermethrin	1	0,05	0,02	ND	ND	ND
	2	0,025	0,02	ND	-	ND
Endosulfan ($\alpha+\beta$)	1	1	0,14	0,006	0,002	0,001
	2	0,5	0,02	0,002	-	0,002
Carbofuran	2	0,35	0,085	0,053	-	ND

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IAEA-SM-354/84P

INTERACTION BETWEEN PESTICIDES AND HUMIC SUBSTANCES FROM TROPICAL COASTAL LAGOONS[1]

XA9951992

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In the northwest coastal plain of Mexico there are several coastal lagoons (375,000 ha) of great ecologic and economic importance and also the most important and technified agricultural fields (1,500,000 ha irrigated fields) of the country. In these fields very large amounts of pesticides are applied each year and their residues enter the lagoons mainly by the agricultural drainage [3].

Those lagoons are surrounded by mangroves which are an important source of humic substances (HS), the HS reach concentrations of 100 mg/L during the rainy season [1] and can interact with pesticide residues affecting, among others, the solubility, sorption, bioaccumulation and bioavailability of the pesticides through the formation of complex molecules [2]. As with other type of contaminants the study of the interactions between pesticides and HS is of great importance for the appropriate management of coastal areas impacted by agricultural runoff.

The HS that enter the lagoons with freshwater runoff tend to precipitate with salinity. Experiments were done in laboratory to determine the effect of HS (isolated from coastal lagoons) and humic acids (HA) (Aldrich) on the partition of selected pesticides between water and sediment phases. Due to the accurate results obtained with radio-labelled compounds, ^{14}C-labelled pesticides were used for the experiments. The selected pesticides were: chlorpyrifos (o,o-di-[1-^{14}C]ethyl o-3,5,6-trichloro-2-pyridil phosphorotioate), DDT (1,1,1-trichloro-2,2-bis(p-chloro-[ring-U-^{14}C]-phenyl)ethane) and parathion (o,o-diethyl o-4-nitro-[ring-U-^{14}C]-phenyl phosphorotioate).

The ^{14}C-labelled pesticides were spiked in separate glass jars with sea water (38 o/oo) and then, in different experiments, aliquots of a distilled water stock solution of HS and HA were added. After one hour at room temperature the jars were centrifuged to separate water and the pellets of precipitated humics. Absorbance (380 nm) of the supernatants was recorded to evaluate the percentage of precipitated humics. The HS and HA pellets were extracted with hexane in a sonic bath and centrifuged again. The ^{14}C radioactivity (dpm) of the pellets, of the hexane fraction and of the aqueous fraction were measured with liquid scintillation counter (Packard 2100TR) to determine the amounts of ^{14}C-pesticides bonded to the precipitated humics.

The results obtained indicate that from 70 to 90% of the HS and HA that enter into sea water precipitate, with 10 to 30% of them remaining in solution. After gel filtration chromatography (Sephadex G-15) of aliquots of HS and HA stock solutions, it seems that the precipitated humics are high molecular compounds and the soluble humics are low molecular weight compounds (~200 Daltons).

The percentage of activity measured in the pellets (Figs. 1-2) indicate that a significant percentage of DDT is strongly bond to the humics precipitate (76% for HA and 36% for HS), probably due to its low water solubility. For chlorpyrifos, that has also a low solubility in water, there is an important percentage of compound bonded to the humics that precipitate (32% for HA and 13% for HS) and for parathion, that has a high solubility in water, there was a small amount of pesticide bonded to the humics precipitate (8% for both HA and HS).

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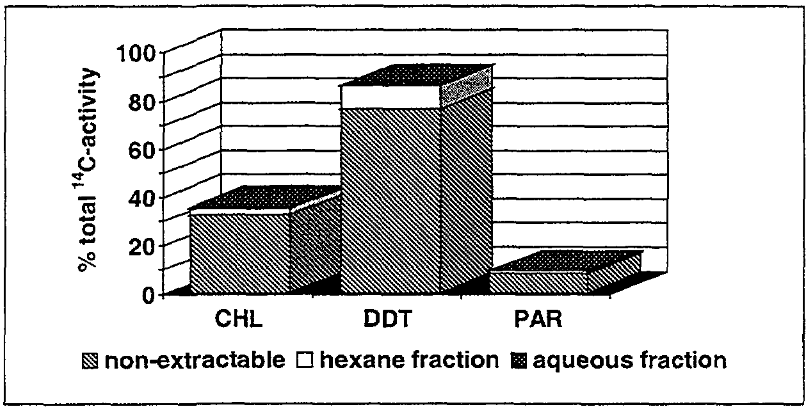

FIG. 1. Percentage of total activity of ^{14}C-labelled pesticides in humic acids pellet. CHL = chlorpyrifos; PAR=parathion.

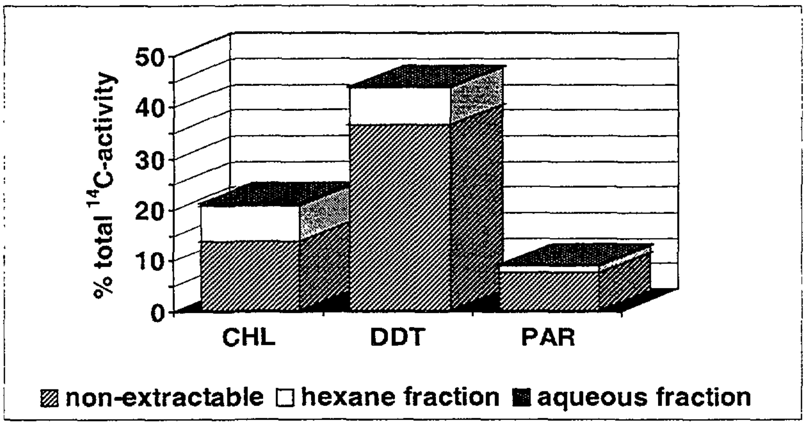

FIG. 2. Percentage of total activity of ^{14}C-labelled pesticides in lagoon humic substances pellet. CHL = chlorpyrifos; PAR=parathion.

With the results obtained we concluded that significant percentages of certain pesticides that enter coastal lagoons, with brackish or marine conditions, can form complex compounds with HS which precipitate. Evidently the pesticides-HS complexes will have different dynamics in the environment (sorption, degradation, partition, bioavailability, etc.) than pesticides alone.

The presence of HS in coastal waters seems to prevent, to a certain extent, pesticide pollution through elimination of pesticides by sequestering them in the sedimentary phase. Preliminary results of mussels (*Mytillus galoprovincialis*) exposed to ^{14}C-labelled pesticides in the presence and absence of HS, indicate that uptake of pesticides by the organisms is less in the presence of HS (González-Farias *et al.*, in prep.). With these results its evident that HS tend to diminish the impact of pesticides over aquatic ecosystems and confirms the results of other authors [4].

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IAEA-SM-354/85P

ORGANOCHLORINE RESIDUES IN SOME DOLPHIN SPECIMENS STRANDED ON SOUTHERN ADRIATIC COASTS (ITALY)

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Organochlorine compounds such as those pertaining to the family of DDTs and polychlorinated biphenyls are extremely persistent and difficult to degrade. Despite the fact that these compounds have been forbidden in many developed countries and their worldwide production and use have drastically decreased in recent years, at present they are widely spread and have become ubiquitous contaminants in the ecosystem. Because most organochlorine contaminants are extremely lipophilic and resistant to degradation, they tend to concentrate and biomagnificate through food webs. Marine mammals such as seals and cetaceans are known to accumulate higher levels of these compounds in their subcutaneous fat or lipid fraction of tissues because they are situated at the highest trophic level in marine ecosystems. A large number of organochlorine pollution surveys in cetaceans of both *T. truncatus* and *S. coeruleoalba* have been carried out, while little information is available on *G. griseus* and *Z. cavirostris*. This paper reports the concentration of PCBs and organochlorine compounds and percentage composition of the different PCB congeners in various tissues from four different species of cetaceans stranded on the Adriatic coast of Italy in July-September 1995.

A total of 10 specimens, all female, (4 *T. truncatus*, average lenght 272 cm, 4 *S. coeruleoalba*, average length 267 cm, 1 *G. griseus*, length 311 cm, 1 *Z. cavirostris*, length 530 cm) were examined in this study. Animal dissection provided samples of blubber, muscle as well as of the following organs: brain, kidney, liver, lung. All samples were frozen at -18 °C until their analysis. Aliquots (2-5 g) of the homogenized samples were ground with Na_2SO_4 and extracted following the procedures described by Erney [1]. After gravimetric analysis of fat content the extracts were treated with $H_{\square}SO_{\square}$ conc. for the clean-up [2] and injected into a gas chromatograph. Gas chromatograph (Carlo Erba-HRGC-5300) equipped with a ^{63}Ni electron capture detector (ECD-400), and splitless injection tecnique was used for the quantification of PCBs, HCB and DDTs (o,p'-DDT, p,p'-DDD, p,p'-DDE and p,p'-DDT). The column consisted of a fused silica capillary SPB-608 Supelco (length = 30 mt, i.d. = 0.25 mm). Quantification of PCB congeners was performed using gas chromatograph-mass spectrometer (Fisons-GC-MS 800). PCB congeners were determined by Selected Ion Monitoring (SIR) at m/e 326, 360, 394 and 428 for penta-, hexa-, hepta- and octachlorobiphenyls, respectively. Helium was used as the carrier gas, while nitrogen was the make-up gas.

The analytical results are given in table 1. In each tissue of *T. truncatus*, *S. coeruleoalba* and *G. griseus* analysed the highest concentrations are of PCBs followed by DDTs and HCB. *Z. cavirostris* shows, on the contrary, higher levels of DDTs with respect to PCBs. In all cases the highest concentrations of the examined organochlorine compounds occurs in blubber followed by liver and kidney in accordance with the greater percentage of total lipids extracts. The other organs contained different pollutant levels related to the different species. Brain showing rather high lipid contents respect to liver and kidney, was much lower in the levels of PCBs and DDTs compounds. This can be explained by the different lipid composition of the brain rich, mainly, in phospholipids or total cholesterol (90%) [3] with respect to other organs. The percentage composition of the different PCB congeners shows a greater hexachlorobiphenyls percentage followed in decreasing order by hepta, penta and octachlorobiphenyls. The low values of DDTs/PCBs ratios found in *T. truncatus* may be related to a greater birth frequence and to a longer lactation period typical of this species [4] with respect to *S. coeruleoalba*. Infact lactation and parturition are considered to be major routes of excretion of chlorinated hydrocarbons, chiefly of DDTs, in cetaceans [5] while as other species litterature lacks data on reproductive biology and on pollutan accumulation.

TABLE I. % LIPID CONTENT, CONCENTRATION OF HCB, DDTS, PCBS (μg/kg wet wt.), % CHLOROBIPHENYL CONGENERS AND DDTs/PCBs RATIOS.

T. t.	lipid %	HCB	DDTs	PCBs	% penta	% hexa	% hepta	% octa	DDTs/PCBs
blubber	38.50	58.4±4.51	4457±346	17950 ±1425	9.21	64.78	25.30	0.71	0.25
liver	3.01	3±0.37	306±22	1300±56	12.89	60.16	26.72	0.44	0.23
muscle	0.16	0.4±0.25	15±5	108±15	11.95	61.51	26.29	0.30	0.13
kidney	2.37	7.6±0.80	192±11	1047±64	15.01	58.57	26.21	0.39	0.18
lung	0.88	1.4±0.31	53±5	205±15	12.57	58.77	28.53	0.24	0.26
brain	8.07	7.2±0.33	68±7	345±23	20.21	51.93	27.58	0.28	0.20
S. c.									
blubber	76.02	77.9±6.61	34390±3210	39070±3629	14.49	59.99	25.04	0.48	0.88
liver	2.50	6.4±0.45	1184±171	1835±198	14.07	56.53	28.65	0.75	0.64
muscle	1.08	2.7±0.31	155±13	273±22	15.34	58.19	26.24	0.36	0.57
kidney	1.29	1.8±0.37	618±24	765±57	14.81	58.67	26.63	0.34	0.81
lung	1.20	2.1±0.30	350±47	560±60	16.27	54.39	28.63	0.71	0.62
brain	7.00	5.2±0.25	308±49	594±72	20.11	51.16	28.22	0.53	0.52
G. g.									
blubber	22.96	18.3	4439	8390	17.70	50.05	29.99	2.11	0.53
liver	1.84	2.3	327	414	20.85	47.74	29.11	2.69	0.79
muscle	0.35	0.4	69	122	21.81	48.19	27.76	2.22	0.56
kidney	1.64	1.8	127	253	17.94	50.01	29.72	2.32	0.50
lung	0.66	0.7	43	58	19.55	46.55	32.05	1.84	0.74
brain	7.72	1.8	150	153	24.10	41.81	31.48	2.60	0.98
Z. c.									
blubber	85.32	31.8	42880	30810	16.71	48.28	32.64	2.37	1.39
liver	3.38	1.9	447	362	18.00	51.68	29.78	0.61	1.23
muscle	0.62	0.5	156	120	17.10	50.00	30.92	1.97	1.30
kidney	1.65	0.4	410	292	14.71	57.13	26.42	1.72	1.40
lung	0.40	0.2	22	19	15.61	56.36	26.90	1.13	1.16
brain	12.25	1.9	93	75	20.05	47.13	31.25	0.47	1.24

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IAEA-SM-354/87P

RECENT NORDIC INERCOMPARISON EXERCISES ON RADIOANALYTICAL QA/QC

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Two intercomparison exercises were carried out during 1996-97 under the Nordic Nuclear Safety Research (NKS) Programme. The first exercise [1] dealt with analysis of artificial and natural radionuclides in two sediment samples, one from the Baltic Sea and one from the Kattegat. The measurement techniques included gamma spectrometry and radiochemical procedures followed by alpha spectrometry. The participants comprised 21 laboratories, 14 from the Nordic countries, 6 from the Baltic republics and one from Japan.

Results were submitted for several radionuclides comprising Cs-137, Cs-134, Co-60, Sb-125, Pu-239,240, Pu-238, Am-241, Sr-90, Ra-226, Th-232 and K-40, Pb-210, Po-210 and U-235. The analytical performance of the participants was evaluated for those radionuclides where six or more data sets were received. Statistical tests were made to see if individual results agreed with overall average radionuclide concentrations in the two sediment materials within target standard deviations. The results of the Cs-137 results for the Kattegat sample is shown in the graph below.
It is noteworthy that with the exception of Co-60 the performance criteria were not met in 20-40% of the data sets for the relatively straightforward gamma-spectrometric analyses of Cs-137, Cs-134, Ra-226, Th-232 and K-40. For the more complicated radiochemical analyses of plutonium isotopes only 13% of the data sets did not meet the performance criteria. The test of the overall analytical performance showed that 61% of the data sets did not meet the combined performance criteria. This shows that there is room for considerable improvement of analytical quality for most of the laboratories that have participated in this intercomparison. The intercomparison exercise has furthermore demonstrated several elementary problems in analytical work such as interchange of samples, mistakes in calculations and correction of background levels.

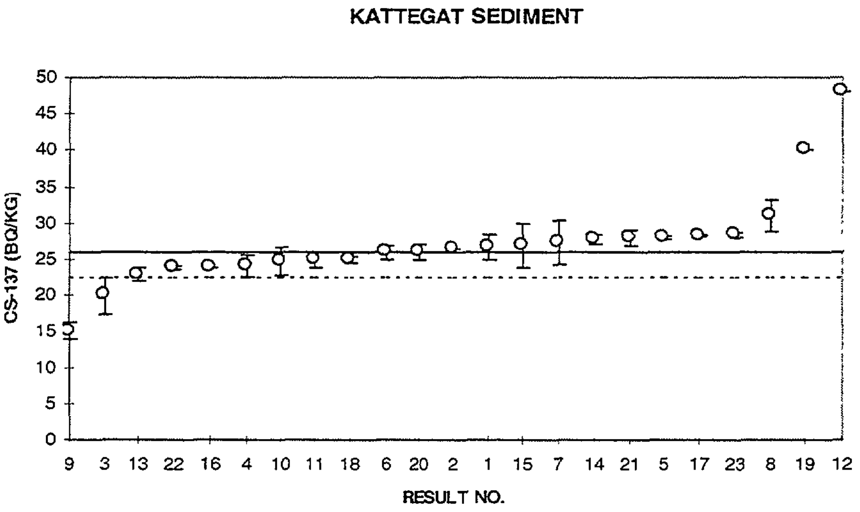

FIG.1 Kattegat Sediment

The second intercomparison [2] covered software for the analysis of Ge gamma spectra and was carried out by testing the quality of calculated areas and associated uncertainties of well-isolated single peaks from IAEA test spectra. The intercomparison comprised tests of precision and accuracy, and furthermore permitted a ranking of the results according to accuracy. Fifteen sets of data were submitted for the intercomparison involving a range of software packages using different methods for calculating peak areas and uncertainties.

The tests of precision showed that only 8 of the 15 data sets show agreement between the calculated and observed variability of the peak areas. Four data sets overestimate and three underestimate the uncertainties of the peak areas significantly. The tests of accuracy have shown that only six data sets demonstrate agreement between calculated peak-area ratios and true values from the IAEA spectra considering the calculated uncertainties. For the remaining nine data sets the accuracies of the calculated peak-area ratios disagree with the true results considering the uncertainties. For one data set the uncertainties are significantly overestimated and for the eight others the uncertainties are underestimated.

Only four of the 15 data sets show both acceptable precision and accuracy, and the accuracies of the other data sets have been tested against the results of one of these sets to provide a ranking between the data sets (figure below). The data sets may be grouped in three categories according to accuracy. Seven data sets show high accuracy, five data sets show average accuracy and three data sets show low accuracy. High accuracy is a factor of 0.6 better than the average accuracy, and the average accuracy is a factor of 2.4 better than the low accuracy. Generally, the data sets based on sophisticated methods for calculating peak areas (e.g. peak fitting) do not show higher accuracy than those based on more simple methods.

The results of the intercomparison show that the quality of results from gamma-spectrometric analyses of radionuclides providing well-isolated single peaks (e.g. ^{137}Cs) vary significantly between software packages. The results furthermore indicate significant effects on the quality from the user of the software.

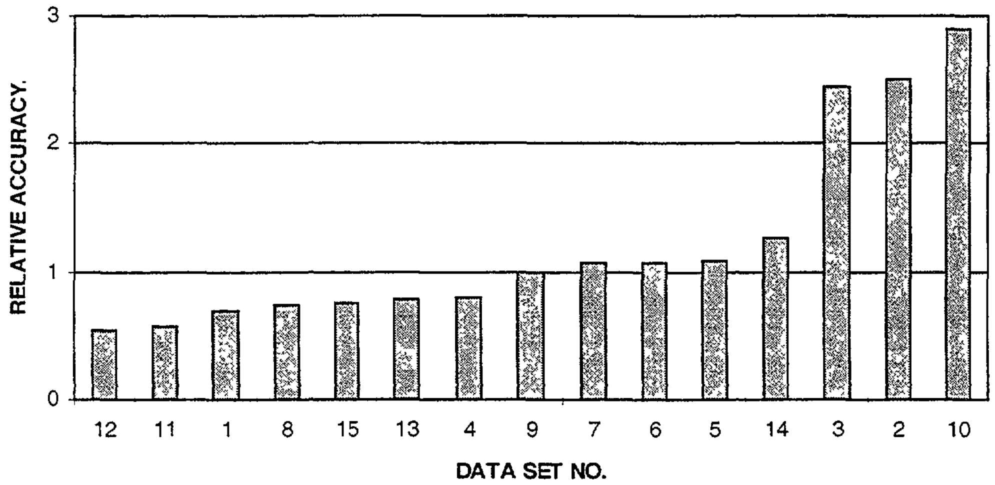

FIG 2. Relative Accuracy

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IAEA-SM-354/91P

QUALITY ASSURANCE PROGRAMME FOR ENVIRONMENTAL RADIOACTIVITY MEASUREMENTS AT THE HONG KONG OBSERVATORY

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The Hong Kong Observatory (HKO)runs an Environmental Radiation Monitoring Programme (ERMP) to monitor the environmental radiation levels in Hong Kong. In the ERMP, about 400 environmental samples are delivered to the HKO Radiation Laboratory each year for alpha, beta and gamma measurements. The quality of the radiation measurements is assured through an internal quality assurance programme and inter-laboratory comparison exercises.

The HKO has participated in the IAEA Intercomparison Runs since 1989. Activity measurements on alpha, beta and gamma emitting radionuclides in eleven IAEA intercomparison samples of clover, soil, sediment, flesh and sea water were conducted from 1989 to 1996, namely IAEA-156, IAEA-352, IAEA-367, IAEA-375, IAEA-134, IAEA-135, IAEA-300, IAEA-315, IAEA-326, IAEA-327 and IAEA-381.

Reports on the first eight intercomparison runs were received. Performance of the HKO in these eight runs was satisfactory except three outliers in two of the runs. The activity concentration of Am-241 and K-40 in IAEA-134 and Pb-214 in IAEA-315 were too high:the respective mean reporting values were 46 ± 5, 290 ± 14 and 20 ± 2 Bq/kg as compared to the respective range of accepted laboratory averages of 32.0 – 44.6, 160.5 – 269 and 8.0 – 17.2 Bq/kg. Table I summaries HKO's reporting values of these radionuclides and the corresponding statistics given in the reports.

TABLE I. HKO'S REPORTING VALUES OF ACTIVITY CONCENTRATION CLASSIFIED AS OUTLIERS AND THE CORRESPONDING STATISTICS GIVEN IN THE REPORTS OF THE IAEA INTERCOMPARISON RUNS

Sample Code	IAEA-134	IAEA-134	IAEA-315
Radionuclide	Am-241	K-40	Pb-214
Median of accepted values	38.15	212	13
Confidence interval at significant level 0.05	35.0 – 39.4	196 - 240	12.0 – 14.7
Range of accepted laboratory averages	32.0 – 44.6	160.5 – 269.0	8.0 – 17.2
HKO's mean reporting value	46 ± 5	290 ± 14	20 ± 2

Review of the two intercomparison runs showed that the unsatisfactory reporting values for K-40 and Pb-214 arose in the process of background subtraction and that for Am-241 arose in the process of calibration of the gamma spectrometry system.

For IAEA-134, the background measurement was conducted on 21 September 1992 while the five sample measurements were conducted from 22 September to 4 November 1992. The gross activity concentrations of K-40 obtained in the five sample measurements varied from 215 to 304 Bq/kg. The large variation might be due to fluctuation in background values of K-40 for the five sample measurements. This showed that more updated background value should be used for each sample measurement. Furthermore, it was found that a wrong background value of K-40 was used to perform background subtraction for one of the sample spectrum. Incidentally, this mistake escaped the notice of the quality controlling officer before result submission.

If the correct background value was used, the reporting value for K-40 should be 259 Bq/kg which would be within the range of accepted values.

For IAEA-315, the background measurement was conducted on 26 April 1993 while the four sample measurements were conducted from 12 to 26 May 1993. Again, the background value was not updated enough for background subtraction. For such a low activity concentration of Pb-214 in the sample (about 15 Bq/kg), a small change in the radon level in the environment would have significant effect to the gross activity concentration of Pb-214. Furthermore, the counting time of 55000 seconds for the background measurement was found not long enough to obtain good statistics for all gamma peaks of Pb-214. In fact, only the highest yield gamma peak of 351.87 keV could be identified in the background gamma spectrum. Other lower yield gamma peaks of Pb-214 could not be identified due to insufficient counts. Background value of Pb-214 determined based on only one of its gamma peaks definitely would not be of high precision. Use of outdated and high uncertainty background value for background subtraction resulted in the unsatisfactory value of Pb-214.

In IAEA-134, the 59.54 keV gamma peak of AM-241 was used to determine its activity concentration. However, the high purity germanium detector of the gamma spectrometry system was only calibrated down to 88 keV using mixed radionuclide standard solution supplied by Amersham International plc. The efficiency at 59.54 keV used for the determination of activity concentration of Am-241 was only an extrapolated value. Its uncertainty would most probably be the cause for the unsatisfactory reporting value of Am-241.

The above findings prompted the improvement of quality assurance procedures in the Radiation Laboratory of the HKO :

(a) background values should be updated as frequently as possible to ensure that both background and sample measurements are under similar environmental conditions;

(b) both background and sample measurement time should be sufficiently long to eliminate short term background fluctuation and to obtain background values of higher precision;

(c) standard solutions with gamma peaks of energy lower than 80 keV, such as Am-241 itself, Ba-133 or I-129 should be added to the generally used mixed nuclide standard solution for calibration if activity concentration of AM-241 has to be determined; and

(d) all measurement results should be cross-checked by professional staff after quality assurance by laboratory staff before reporting.

It is therefore concluded that participation in intercomparison exercise is an invaluable part of quality assurance in radioactivity measurements and the HKO will continue to participate in the IAEA Intercomparison Runs.

IAEA-SM-354/92P

RECENT RESULTS IN MODELING Ge-GAMMA RAY SPECTROMETRY MEASUREMENTS

XA9951996

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Previous work [1] on modeling Ge-gamma ray spectrometry measurements has been extended. A dedicated computer software, called GESPECOR, has been developed to assist in the assay of gamma radioactivity of environmental samples. Using GESPECOR, full energy peak efficiency (FEPE) and efficiency correction factors due to self-attenuation (Fa) and due to coincidence summing effects (Fc) can be evaluated for a variety of detectors [p or n type closed end coaxial HPGe, well-type HPGE, Ge(Li)] and sample geometry (point, cylinder, Marinelli beaker, sphere, ring). Several standard matrices are predefined and can be selected for typical environmental samples; alternatively a specific sample composition and density can be used, when pertinent data are available.

The core of the software is a realistic Monte Carlo computation, tailored specifically for an efficient simulation of the processes involved in gamma-ray spectrometry. Recent work on the software targeted both on the improvement of the model and on the development of a more flexible, user friendly interface. On the model side, the detector is parameterized by the radius and length of the crystal, of the inner hole (or contact), by the thickness of the dead layers, by the dimensions and materials of the detector holder, end cap and entrance window, by the position inside the end cap. The geometry modules were extended to include the case of detectors with rounded edges; a possible misalignment of the detector in the end cap (as revealed by the X-ray photograph of several detectors) can be taken into account. The simulation of the bremsstrahlung emission and the transport of the characteristic X-rays were improved. On the other side, besides simple interfaces used to prepare input data files (for the detector, sample geometry, shield geometry, and for various materials), a new, more complex module, called INPEN, was added. By this module the decay data for the nuclide of interest are read from the KORDATEN library [2] and the value of the conditional emission probability for various sets of photons (cascading gamma photons, X-rays following internal conversion or electron capture decay, annihilation quanta in beta+ decays) is evaluated. By using INPEN the rather specialized decay data required for computing the coincidence summing corrections are automatically evaluated for any transition belonging to a set of approx. 100 nuclides.

The validity of the computations of the FEPE was established by numerous checks against precisely measured values of the efficiency for a variety of detectors and typical measurement conditions. If accurate detector data are available and disturbing phenomena, such as incomplete charge collection are absent, the accuracy of the computations is better than 5%.

Self-attenuation corrections, applied to compensate the effect of differences in matrix and density between the calibration sources and the actual samples, can be computed with a better accuracy than FEPE, as Fa is less sensitive to the inaccuracy of the detector data [3]. In GESPECOR self-attenuation corrections are evaluated with a fast algorithm; after a preliminary Monte Carlo computation, the Fa values can be used as stand alone correction factors, or can be integrated in the gamma-ray spectrometry analysis program. A new program, dealing specifically with the case of very high attenuation, was included in the GESPECOR package. In the case of very high attenuation the accuracy is better than 5% and is much better in common experimental situations.

As a consequence of the trend to use very high efficiency detectors, important coincidence summing effects may arise. For specific nuclides, measured in the well-type detector geometry, the change in the value of the efficiency due to coincidence effects can be a factor of 10 [4]. A powerful software for evaluating the values of the Fc has been implemented in GESPECOR. In the computations higher order coincidences and angular correlation are included and a realistic simulation of the total efficiency for elementary emission points distributed in the volume of extended sources is carried out. The accuracy of the values of the coincidence correction factor is 2 - 5% in the case of measurements with conventional HPGe detectors, and from 5% (for nuclides with simple decay schemes) to 15% (for nuclides with complex decay schemes and important higher order corrections) in the case of measurement in the well-type detector geometry.

Some comparisons between the computations and precise experimental data are presented in Fig. 1.

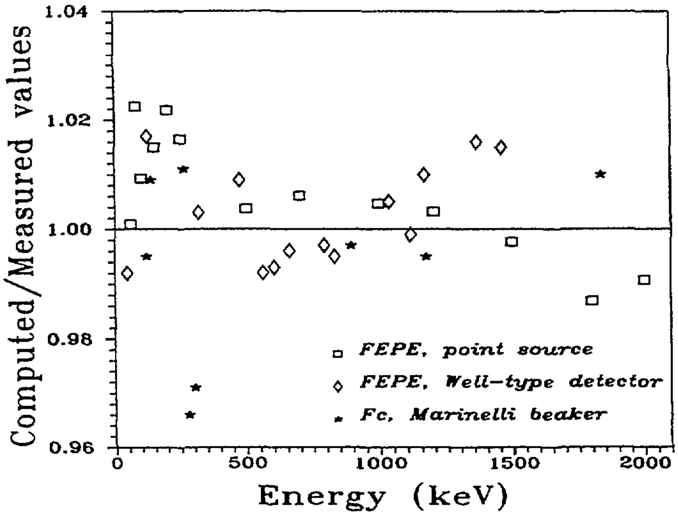

FIG. 1. Computed / Measured values of FEPE (point source + conventional HPGe detector and cylindrical source + well-type HPGe detector) and of Fc (Se-75, Co-60, Y-88, Marinelli beaker source).

First, the ratio of the computed values of the FEPE to the measured values for a point source placed at 10 cm above the end cap of a 124 cm^3 HPGe detector is displayed. Detector data provided by the supplier together with information available from an X-ray photograph of the detector have been used. The effect of the rounded edges of the detector and of the slight misalignment of the detector with respect to the symmetry axis of the end cap (visible on the X-ray photograph) was included in the computations.

On the same figure the ratio of the computed values of FEPE to the measured values for a cylindric sample measured in the well of a HPGe well type detector with a crystal volume of 350 cm^3 is also presented.

A last example is the ratio of the computed values of the coincidence correction factor to the measured values in the case of a 1l solution measured in the Marinelli beaker geometry with a HPGe detector with a relative efficiency equal to 50%. In Fig. 1 the results for the peaks of the nuclides Se-75, Co-60 and Y-88 have been included.

In conclusion, GESPECOR can be successfully applied in gamma-ray spectrometry measurement of environmental samples.

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DEVELOPMENT OF AN UNDERWATER CHERENKOV DETECTOR TO REVEAL SOURCES OF TECHNOGENIC RADIONUCLIDES

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Nowadays for monitoring marine radioactive contamination much use is made of underwater scintillation detectors permitting in situ detection of radionuclides from a surface ship, as well as manned and unmanned submersibles [1]. Detection of gamma-emitting radionuclides using the scintillation underwater detectors presents no special problems. The problem is revealing of nuclides, when their beta decay is not accompanied by gamma radiation. Primarily it concerns the most ecologically significant strontium-90 nuclide. Since no in situ measurement methods for detecting low concentrations of beta emitting nuclides are available, as a rule, laboratory methods of radiochemical sample analysis are employed, being very laborious and time-consuming.

The major difference of the Cherenkov underwater detector (Fig. 1) from a scintillation detector is that its operation does not require a primary transducer (scintillator). Detected particle energy conversion into a light flash occurs directly in sea water (radiator) due to the Cherenkov effect [2]. Consequently, photoreceiver of the underwater Cherenkov detector registers light[1] from radiator of actually infinite volume. The circumstance is of principle importance, as it permits attaining the utmost sensitivity in case of the minimal overall dimensions and weight of detecting equipment.

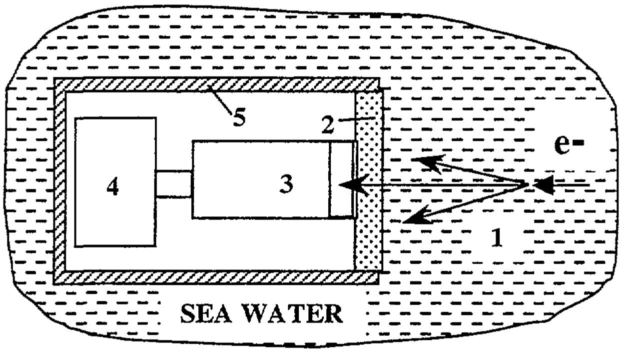

Fig.1 Structural schematic diagram of the underwater Cherenkov detector;
(1) Cherenkov radiation; (2) transparent inlet window; (3) photoreceiver;
(4) electronic module; (5) high-strength capsule.

However, high sensitivity of the Cherenkov radiation underwater detector can only be achieved by suppressing the interfering effect of sea water natural light background. The main components of the light background in sea water are the light of astronomical sources (the Sun, the Moon, the sky and stars), bioluminescence and Cherenkov’s radiation emitted by ^{40}K natural radioactive element. The sunlight is the most powerful source in the light background, its intensity in the daytime in near the surface waters exceeding by many orders the Cherenkov radiation level resulting from ^{40}K radiation.

To assure a high sensitivity of underwater Cherenkov detector a method of the light background suppression has been developed based on optical filtration of light fluxes by the wavelength with due regard for differences in spectral characteristics of the Cherenkov radiation and atmospheric light, as well as optimal combination of optical and geometrical parameters of the detector photoreceiver basic components [3]. The spectral sensitivity range of the

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[1] for electrons the threshold energy of the Cherenkov radiation in sea water amounts to 0.25 MeV.

Cherenkov detector is concentrated at the band of 220-300 nm *(Fig. 2)*. When passing to the spectrum visible range, the sensitivity decreases abruptly. The sensitivity drop occurs in such a way that atmospheric light flux integral values at the output from the detector can not be distinguished, at the background of statistical fluctuations of the Cherenkov radiation integral values, from the natural potassium-40 radionuclide present in sea water.

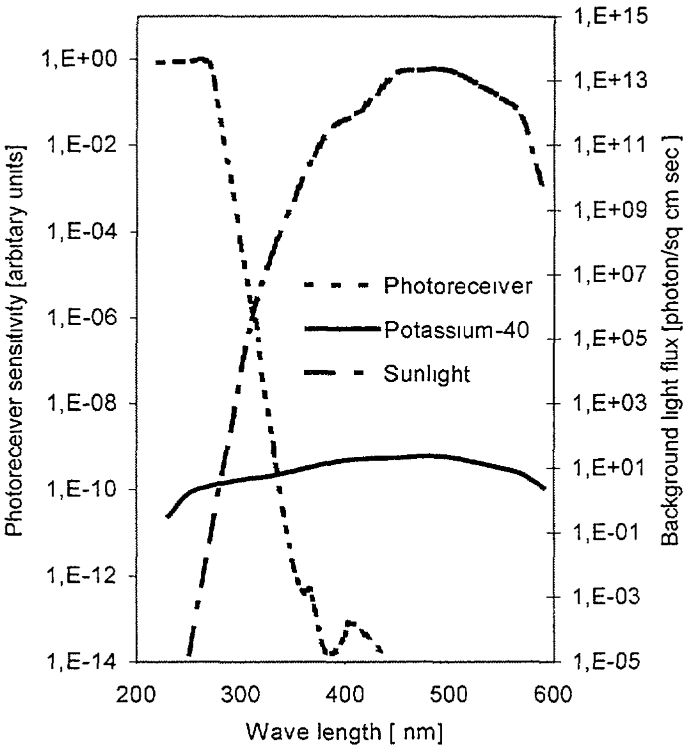

Fig.2 Spectral characteristics of photoreceiver and underwater light background.

Practical implementation of the suggested method, i.e. the light background suppression, is achieved by using a solar-blind filter in the photoreceiver, incorporating an air-isolated alkali metal layer deposited on a transparent substrate in combination with a photoelectric multiplier using either TeCs or TeRb photocathode. Besides, the solar-blind filter contains an additional interference filter made from materials, which are transparent in the working range of the spectrum.

Our estimates and results of preliminary model experiments show that the threshold sensitivity of the detector module for ^{90}Sr + ^{90}Y nuclides in near the surface layer of sea water under the most unfavorable conditions will make up approximately 400 Bq/m^3 if the measurement duration is 10 000 s.

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HERBICIDES FROM THE CHARENTE RIVER AND THE ESTUARINE ZONE (MARENNES-OLERON) TO THE COASTAL SEAWATER

XA9951998

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Spatial distribution of herbicides was investigated in the fluvial section, the estuary of the Charente river and the coastal zone (Marennes-Oléron). The fluvio-estuarine zone is the site of agricultural activities on drained grounds (cereals, forage) and aquaculture-beds (oyster- and mussel-beds) on reclaimed marshes sensitive to continental contributions of the Charente river and the entire complex system of fresh-water canals pouring into the coastal waters.

Monthly samplings were performed on a fluvial section from Angoulème to Saintes, at Chalonne, Nersac, Sireuil, Bourg and Brives from 1993 onwards. Estuarine and coastal sea-waters were sampled during two cruises in May 1991 and February 1992.

Monitoring of trace levels of phenylurea and chlorotriazine was performed on river, estuarine and coastal seawater by off-line and on-line preconcentration techniques using reversed-phase chromatography and UV diode array detection and sometimes electrochemical detection (detection limit 10-50 ng/l).

Fluvial section (from Angoulème to Saintes). Atrazine, simazine, and DEA are continuously present all year round (≈ 200 ng/l). Higher concentrations were observed from April to July and can peak at up to 700 ng/l when stored herbicides are flushed out from agricultural soils by rainfall. Significant but erratic amounts of diuron, isoproturon and linuron are found, corresponding to local sources of contamination.

Fluxes of atrazine, simazine and DEA were evaluated from four years' worth of monthly samplings gathered upstream of Saintes. Large variations of the desethylatrazine/atrazine ratios (DAR) were observed since 1994, from <1 to 10, depending on the season and the climatic conditions

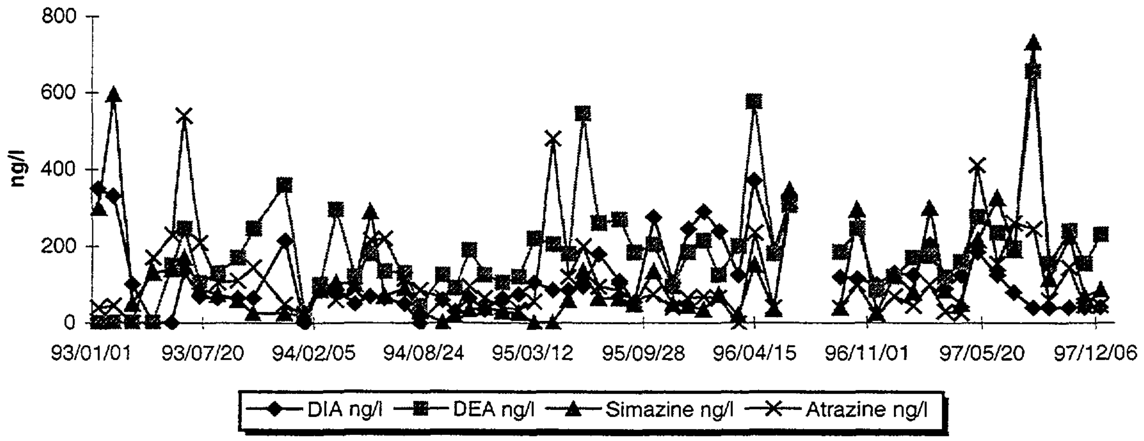

FIG. 1. Concentration of DEA, DIA, simazine and atrazine in runoff from the Charente river at Brives for 1993-1997

TABLE I. YEARLY FLUXES OF DIA, DEA, ATRAZINE AND SIMAZINE

	DIA (kg/y)	DEA (kg/y)	Atrazine (kg/y)	Simazine (kg/y)
1993	235	315	215	185
1994	160	330	220	195
1995	205	300	135	105

Yearly fluxes (kg/y) of atrazine, simazine and their metabolites (DEA and DIA) exported were estimated at Brives from monthly measurements and daily average flow rates (Table I). Exports of atrazine and simazine occur chiefly in the April - July period and can represent 50 to 70 % of the annual flow. 60 to 80 % of the metabolized form (DIA and DEA) are transported during autumn and winter. 1995 is distinguished from previous years by the fact that flow rates are weak from May to October. There is very little herbicide carried along (surface flow). During the late fall rains, replenishment of the Charente river occurs, generating a transfer of herbicides from soils to the river. From the inner and the outer estuary of the Charente river, atrazine, simazine, desethylatrazine and diuron concentrations were found, dependent on sampling location and water salinity at two key-periods of the hydrological cycle (spring and winter). Atrazine, simazine and DEA show conservative behaviour in contrast to diuron.

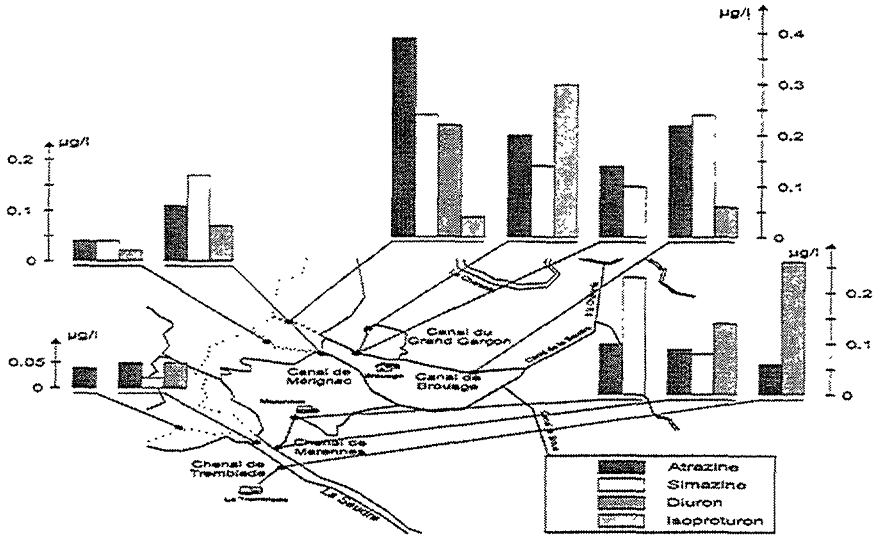

FIG 2. Concentration of triazines and phenylureas in sea-water and drainage canals (91/05/04)

In drainage canals (Brouage, Charras, Marennes), high concentrations of atrazine and simazine were observed in freshwater (atrazine: 7500ng/l, 93/06/21) during the sampling period (April-August 1991).This situation may lead locally to sharp increases in the concentrations of herbicides in coastal seawater (atrazine:400 ng/l; diuron:200 ng/l) when the fresh water is flushed out from the canals into the sea (Fig. 2). This three-year assessment, these investigations points out that the flux of metabolites (DEA and DIA) is clearly greater than their precursors (simazine and atrazine). The influence of the Charente Maritime (Marennes-Oléron) reclaimed marshes' canals and channels on coastal water contamination was observed from high concentrations of atrazine, simazine, diuron and isoproturon in the coastal waters, a phenomenon that cannot be explained by the contributions of the Charente river alone.

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INTERCOMPARISON STUDY OF SAMPLING METHODS FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) IN SEAWATER

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The determination of organic pollutants in seawater is a serious problem, as their concentrations in the water column are typical in the fg - ng/L range. Available methods therefore includes extensive sampling and laboratory work. The development of simple sampling techniques for organochlorines (e.g. passive sampling with semipermeable membrane device (SPMD), mussel watch) is required.

Three methods for the measurement of trace organochlorines in seawater were investigated 1) the filtration (GF/F) and extraction (XAD-2 resin) of seawater with an in-situ pumping system [1], 2) biological-accumulation by mussels (mytilus edulis) and 3) passive sampling with SPMD.

The study was carried out over a period of 8 weeks in September 1997. The mussels and the SPMD were deployed side by side at 15 m depth in the Kiel Bay (Baltic Sea). Subsamples (triple) were taken every week, at the same time discrete samples with the KISP (Fig. 1) were collected.

The extraction of the material, the sample clean-up procedures and gas chromatographic measurements were carried out by standard methods for the determination of chlorobiphenyls (CB) in seawater [2].

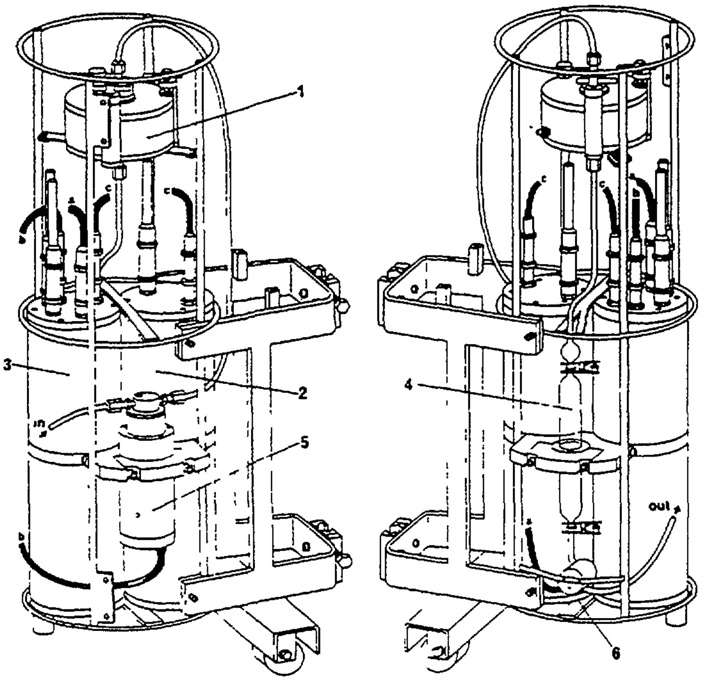

FIG. 1 KIEL in-situ Pump 1: Filter holder, 2: standard power pack housing, 3: housing for electronic, 4: resin holder, 5: pump, 6: flow rate counter, a,b,c: cable connections

The KISP was the only system, that can separate the dissolved and particular forms. Concentration of ZCBS (sum of 17 congeners) in solution varied between 2 - 8 pg/L and in suspension The concentrations of ZCBS in mussels were between 100 - 480 ng/g lipid material, with no obvious trend during the experiment. In comparison the SPMD was less variable at each sample date and between 40 - 55 pg/L. This suggests that suspended organic matter was the dominant carrier for these relatively apolar substances. These concentrations are in the typical range for the Baltic Sea [3].

The concentrations of ΣCBs in mussels were between 100-480 ng/g lipid material with no obvious trend during the experiment. In compaarison the SPMD was less variable at each sample date and show a strong increase (5.8 ng/g lipid after 7 days to 38.5 ng/g lipid after 60 days, corrected with blanks) during sampling period. The blank values of the SPMD were very low (about 1 -2 ng/g) and reproducible. At the end of the experiment the SPMD material and the container was strong covered with algae. This raises the issue that biofouling can affect the SPMD material and the SPMD kinetics.

CB compositions were similar in all sample types, but not identical (Fig. 2.) The strongest contributions in mussels originate from CB No. 138 and 153. The lower chlorinated CBS dominated in solution. The composition in SPMD was most similar to the particulate composition.

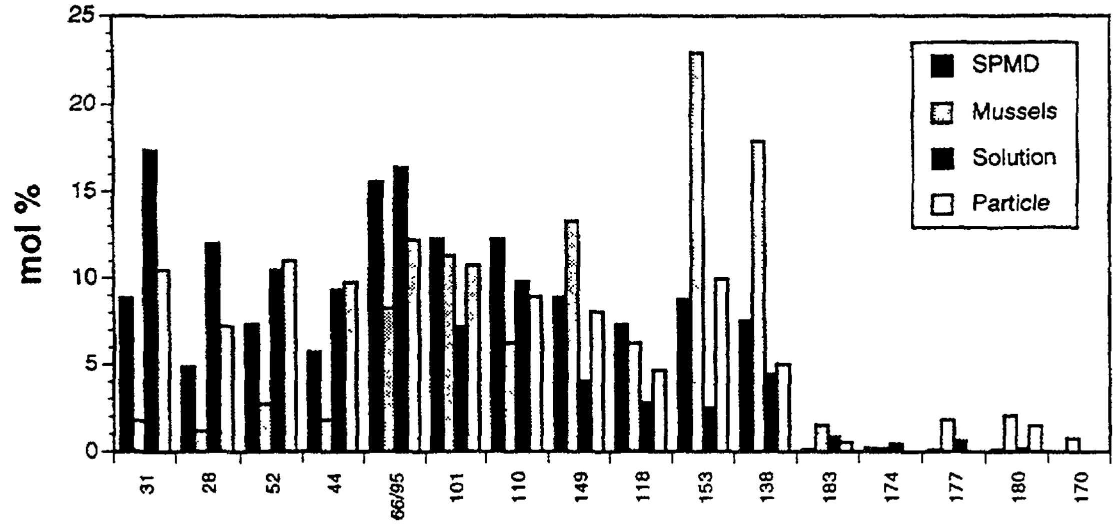

Fig. 2 Mol % contributions of individual CBS to their sum in solution, suspension, mussels and SPMD.

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CONTAMINANTS AND NUTRIENTS IN VARIABLE SEA AREAS (CANVAS) - APPLICATION OF AUTOMATIC MONITORING STATIONS IN THE GERMAN MARINE ENVIRONMENT

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Monitoring is the repeated observation of a parameter in the environment in order to detect environmental pollution or contamination in time and/or space. The monitoring in the marine environment is mostly carried out by means of conventional collection of the samples from research vessels. However, this procedure can only provide data during the period when the research vessel is available. The observation and thus the interpretation of the data is restricted to the time of sampling in particular if the monitoring is to be done in a sea area where the hydrographic parameters S and T are highly variable due to large river discharges and/or high tidal currents. This will also dominate the concentration level of contaminants and nutrients.

Permanent observation of paramaters at sea stations can only be obtained by automatic sampling. The MERMAID technique developed in former projects [1] provides a possibility to run automatic stations within the German MARNET measuring stations to obtain data on nutrients concentration on line and to collect organic micropollutants and the radionuclide ^{137}Cs by solid phase extraction from seawater and subsequent analysis in the laboratory. The BSH MARNET consists of ten stations located in the German Bight sector of the North Sea and the western Baltic.

The hydrography of the German Bight is influenced by the input from Atlantic water through the Channel and by the input from the river systems from Rhine, Ems, Weser and Elbe. In addition, the salinity at a given position is influenced both by tidal currents and wind forces. The input of nutrients and harmful substances into the German Bight occurs primarily from rivers [2]. This input is highly variable in time depending on the river run-off. Nutrients in addition show a strong seasonal dependence due to consumption during phytoplankton production and remineralisation to inorganic constituents during the winter period.

The hydrographic situation in the western Baltic Sea differs slightly from that from the German Bight. This sea area is the transition zone between the North Sea/Kattegat and the Baltic Sea. The high saline water inflow from the North Sea occurs below the halocline. The water outflow of less saline water takes place at the surface layer [3]. This exchange produces a highly variable hydrographic condition at these locations.

During the three years project funded by the German Ministry of Research four stations are equipped with MERMAID technology including automatic pump photometers (APP) to determine Phosphate, Nitrate and Ammonia. Silicate will be measured on one remote station.

On two of the stations an automatic sampler for organic micropollutants (and ^{137}Cs) (ASOM) will be installed. This ASOM collects water samples in a remote controlled manner and retains the organic pollutants on filters and organic solid phase adsorbers. The station will be maintained in a three weeks intervall during winter period and six weeks intervall during summer; during this maintenance the absorber are to be changes for final analysis in the laboratory.

First results from the time series of nutrient and organic micropollutant concentrations has been presented.

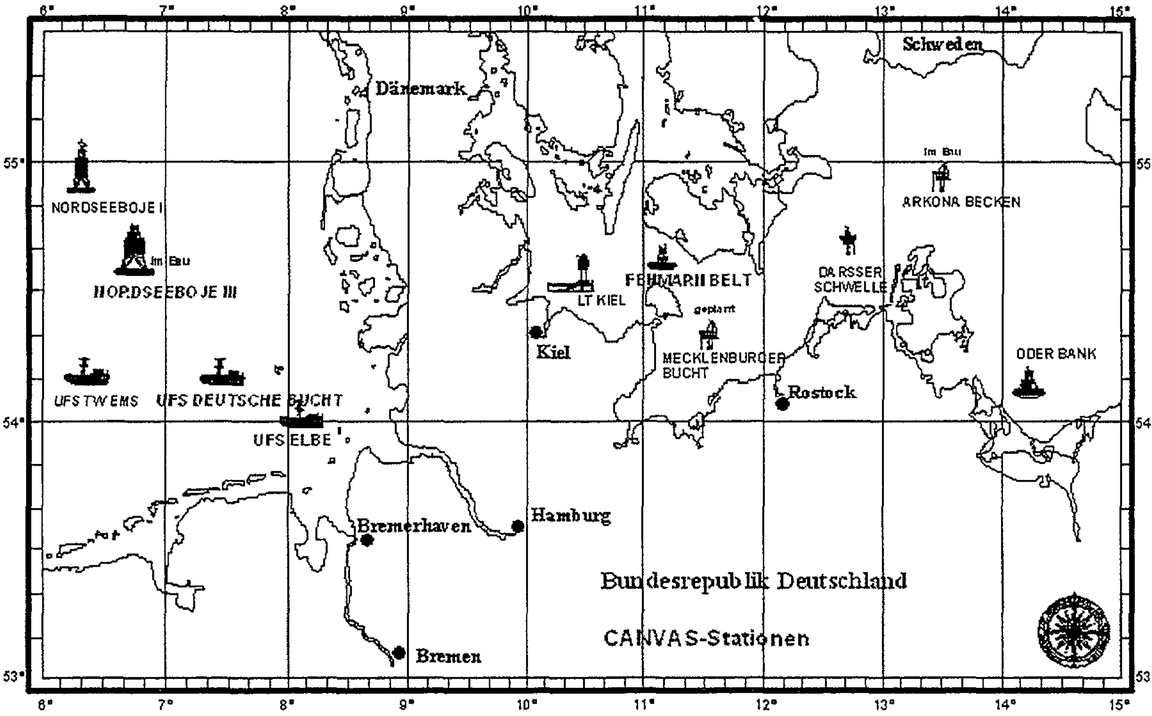

FIG. 1: The locations of the measuring network of the BSH (MARNET). The stations "ELBE", DEUTSCHE BUCHT, NORDSEEBOJE III, and FEHMARN BELT will be equipped with MERMAID components e.g. APPs for nutrient monitoring.

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PARAMETRISATION AND EMPIRICAL MODEL FOR BEDLOAD MOVEMENT IN THE MULTIBAR COASTAL ZONE ON THE BASE OF FIELD RADIOTRACER STUDY

XA9952001

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The near-shore zone is the most interesting sea region is coastal engineering. In this region the most effective changes in coastal morphodynamic takes place due to intensive sediment transport generated by waves and currents. The processes occurring in this zone are of great importance for coast protection and hydrotechnic activities as well as recreation. They are extremely complicated due to their stochastic character in the time and space domain.

The most valuable information concerning the dynamics of bedload transport and its local character is provided by the field surveys. Such investigations are carried out under natural conditions and take into account the characteristic properties of the region.

The subject of the work was the study of bedload movement for the multibar conditions. The aim was determination of the main characteristics of this movement:

- critical. velocities of single grains motion and mass transport beginning;
- thickness of the mobile sediment layer,
- mean velocities of bedload sediment motion,
- intensity of sediment transport.

The field study was carried out in a multibar (4-5 bars) coastal zone 700 m long and about 1000 m wide at Coastal Laboratory near Lubiatowo (southern coast of Baltic sea). Sediment transport in this region was the object of intensive and complex field studies by the use of radiotracer method [1].

The most effective way to investigate the sediment transport processes under natural conditions is a tracer technique. The characteristic advantage of this technique is non-invasive observation and measurement of parameters of the bedload or pollutant transport in Seabed floor. Especially the radioactive tracers provide the most reliable information concerning of examined process due to measurement of nuclear radiation (continuous detection, no sampling necessity). The isotope of ^{192}Ir was used as a radiotracer in the work. The ^{192}Ir was a component of specially prepared glass grains of the diameter of 0,020 - 0,025 cm and density of 2668 kg/m3. The tracer was introduced at selected points of the coastal zone in order to cover its most interesting regions. As a result of interaction of waves and current on the sea bottom, bedload motion was evaluated on the base of measured tracer distribution within a region under test [2].

During the experiment run the basic meteorological and hydraulic parameters were recorded;

- wind (direction and velocity),
- wave (amplitude and period),
- current (direction and velocity).

It has been obtained that the motion of single grains of the bedload appears at the water velocity equal to 8 - 12 cm/s. The staff of mass transport occurs at the water velocity of 30 - 40 cm/s.

Core sample were analysed, and result obtained indicates the stratified structure of bedload transport. The two layers of bedload move with different velocities. The mass transport in the layer of some centimetres occurs simultaneously with the surface motion in the very thin layer (some several diameters of bedload grains). In the cases of small interaction between the wave and the bottom the transport of sediment occurs in the Surface layer only. Relationship between mean velocities of Surface and mass bedload transport and water current velocity was obtained.

The results obtained give the possibility to elaborate empirical model of the global Sediment transport rate for the multibar conditions. The solution of the model for the different conditions has been presented in the form of nomograms [3] Example nomogram have been shown at Fig 1.

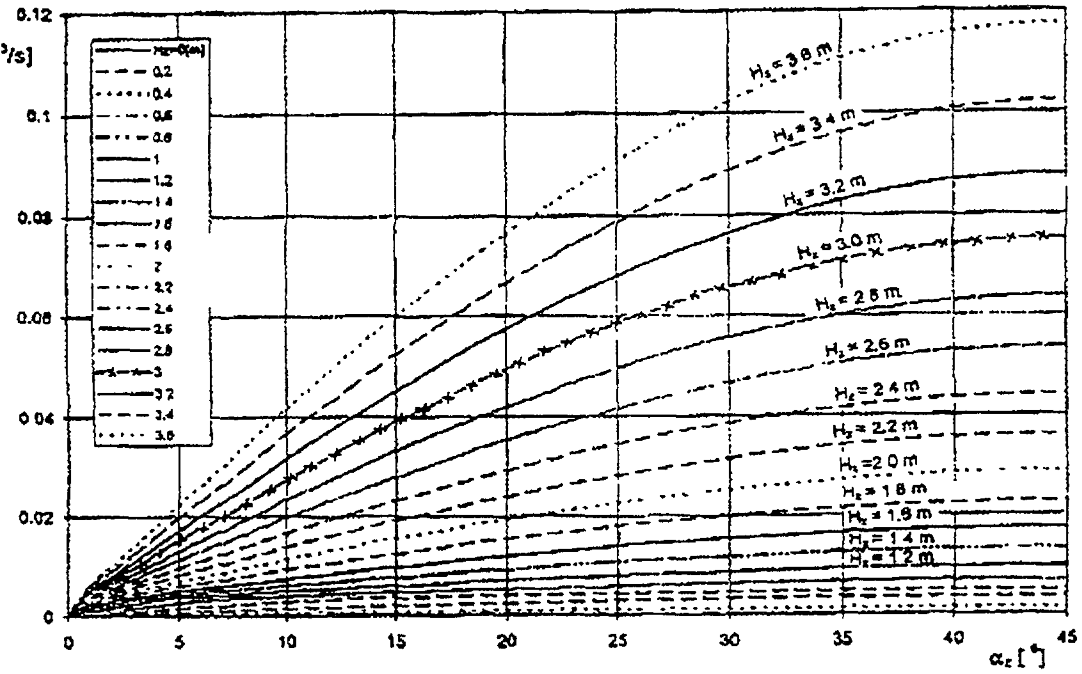

FIG. 1. The global sediment transport Q versus angle of breaking waves α_z for different values of breaking waves height H_z.

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ACCUMULATION OF PETROLEUM HYDROCARBONS IN ZOOPLANKTON OF BANYAS COASTAL WATERS (SYRIA)

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We present in this paper the distribution of petroleum hydrocarbons in seawater and their levels in zooplanktonic samples. Sampling operation was carried our between August 1995 and November 1996 in the coastal area of Banyas city (Eastern Mediterranean). Petroleum hydrocarbons concentrations were: ranged between non detectable values and 16.4 pill in seawater, and between non detectable values and 4304 µ/g dry weight in zooplanktonic samples.

Sea water and zooplanktonic Samples were collected from three oceanographic stations, along the coast of Banyas city (Fig 1); Sampling operations were carried out from August 1995 to November 1996 for seawater, and from December 1995 to November 1996 for zooplankton The different stations were characterized to present different types of pollution; station 3 is located near the discharge effluents of Barij, as refinery.

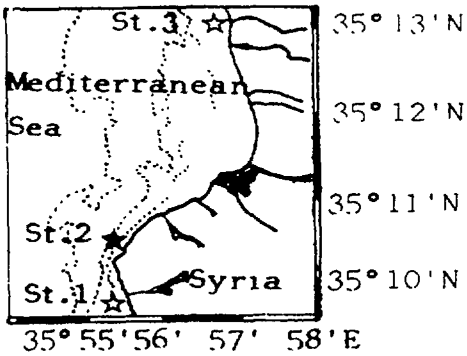

FIG 1: Geographic localisation of different sampling stations

Water samples were collected at 05 meter below water surface, using 2.5 litres pre-cleaned Label-Line water sampler. Dissolved and dispersed petroleum hydrocarbons were extracted with a mixture of n-hexane:(it-chloro methane (50:'10 v),and evaluated by spectrofluorimetric technique; the precision is 5% for a petroleum hydrocarbons concentration of 10/µg. Zooplankton<i samples were collected using a WVP2 net (200 µm); they were filltered on Whatman GF/A pre-treated(I filters at 450°.for 2 hour s and extracted later by a mixture of n-hexane:Acetone (80:20 v.) in Soxhlet [1]. The fluorescence of different extracts were determined using JASI'O Spectrofluorimeter FB-777 and chrysene as an inter-comparison chemical standard.

Petroleum hydrocarbons concentrations were ranged between non detectable values and 16.4 fig/I in seawater (Table I) and between non detectable values and 4304 µg/g dry weight in zooplanktonic samples (Table I), the maximal values were recorded in both water and zooplanktonic samples of station 3, reflecting an important impact of the Banyas refinery's effluents on the coastal ecosystem.

TABLE 1. CONCENTRATIONS OF PETROLEUM HYDROCARBONS IN SEAWATER (µg/l) AND IN ZOOPLANKTON (µg/g DRY WEIGHT) AND SOME RELATED DATA, FOR THE COASTAL AREA OF BANYAS CITY

	Petroleum Hydrocarbons in seawater			Petroleum Hydrocarbons in Zooplankton		
Station	**St. 1**	**St. 2**	**St. 3**	**St. 1**	**St. 2**	**St. 3**
Range	0.00-0.78	0.58-3.22	1.20-16.4	0.0-365.5	48.5-216.5	102-4304
Mean	0.36	1.31	6.07	169.03	116.10	1492.50
Standard Error	0.14	0.39	2.19	94.24	39.37	965.36
Standard Deviation	0.34	0.97	5.35	188.49	78.73	1931.36

The obtained concentrations of petroleum hydrocarbons in seawater are in accordance with those registered by [2] for the coastal area of Banyas city. The level of these pollutants in zooplankton recorded in this study coincide, with the results of [3,4]. The relation between the concentrations of petroleum hydrocarbons in Zooplankton and in seawater is illustrated in Fig. 2.

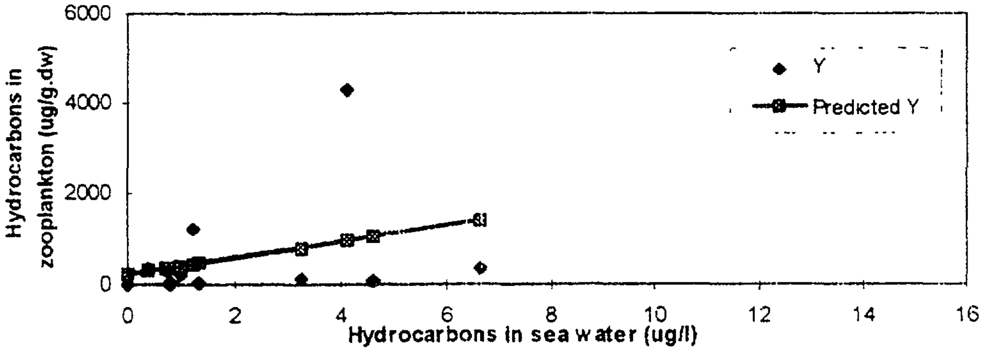

FIG 2: Relation between the concentrations of petroleum hydrocarbons in zooplankton and in seawater (Y=221.68 + 179. 8 x).

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VERTICAL TRANSPORT OF SUSPENDED PARTICULATE TRACE ELEMENTS IN THE NORTH ATLANTIC OCEAN

XA9952003

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Suspended marine particles play a key role in the exchange processes between rapidly sinking particles and seawater because of their large surface area and long residence times. They are involved in the transport processes of rapidly sinking particles (~ 100 m/day) through aggregation and disaggregation. This mechanism results in a net downward transport of suspended particulate trace elements (TE). To provide more information to these processes TE in suspended particulate material (SPM) have been measured on three cruises from 1995 to 1997 along 20°W using a large volume in situ filtration system [1] between 25 m and 4150 m depth in addition to particle flux measurements with sediment traps. These studies were performed under the framework of German JGOFS.

For sampling of suspended particulate TE the Kiel in situ pump (KISP) was used. After sampling, the Nuclepore filters (142 mm, 0.4 µm) were gently washed (to reduce losses of labile compounds) and afterwards stored at -20°C. After drying, the filters were digested in toto with an acid mixture. Final analysis of **Al**, Ca, **Fe**, P and Ti was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and of **Cd**, Co, Cu, **Mn**, **Ni**, Pb, and Zn by electrothermal atomic absorption spectrometry (ETAAS).

From vertical profiles of suspended particulate ^{230}Th concentrations an average vertical transport of SPM of 800 m/yr is estimated for this region by applying the particle flux model [2] The concentration gradients of suspended particulate Al, Fe, Mn, Ni and Cd between 1000 m and 2400 m are interpreted in terms of this result. For three one-year boxes - each corresponding to 800 m depth - suspended particulate TE losses are evaluated. The losses in the boxes might be caused either by the aggregation with rapidly sinking particles or by TE dissolution. In Fig. 1 the exchange between the SPM pool and the rapidly sinking particles has been balanced with the dissolved pool.

The average vertical transport of suspended particulate TE contributes in a major portion to the flux of rapidly sinking particles for Fe (32 %) and Mn (65 %); the particulate Al concentration seems constant with depth (~ 0 % contribution) and the biogenic elements contribute large amounts to the dissolved pool of Ni (56 %) and of Cd (88 %).

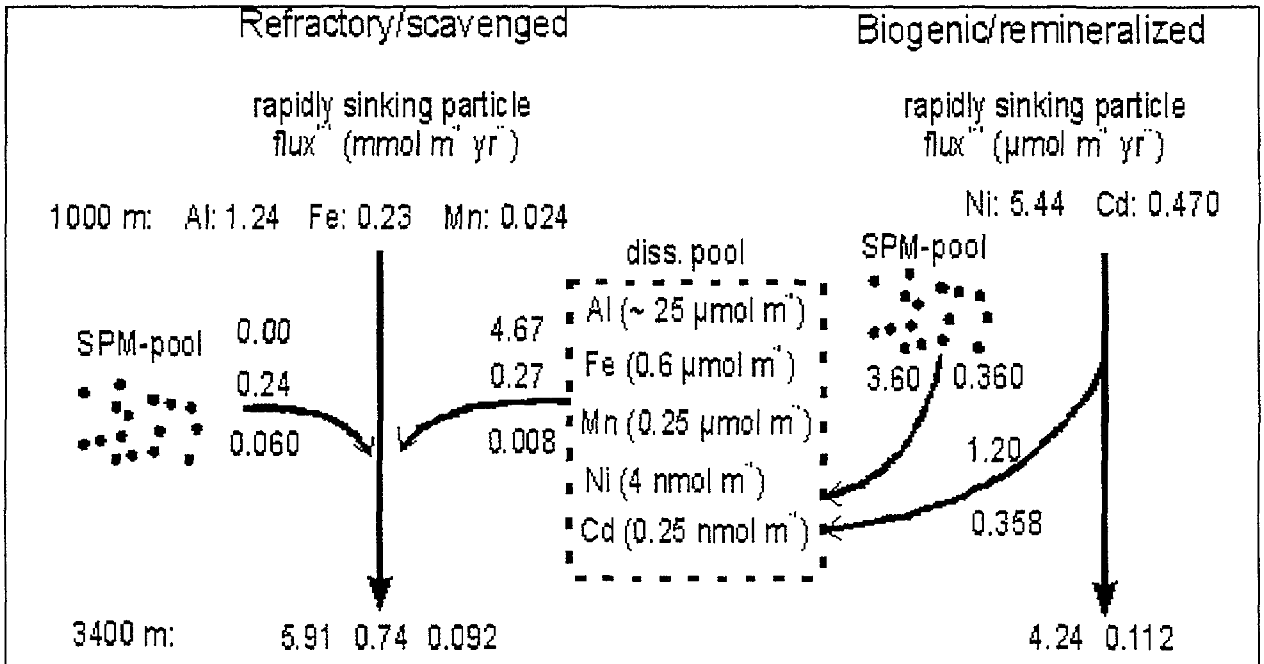

Fig. 1: Exchange processes between rapidly sinking particles, suspended particles and the dissolved pool for selected trace elements at position L2 in mol m^{-2} yr^{-1}.
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GEOCHEMICAL PROCESSES IN THE AQUATIC SYSTEM ON LAND AND THEIR INFLUENCE ON RADIONUCLIDE TRANSFER TO THE OCEANS

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One portion of the marine radionuclide inventory has had a significant residence on land, either in the aquatic system, in the case of liquid discharges of nuclear installations or in the terrestrial system in the case of atmospheric deposition. Migration of theses radionuclides to the oceans is controlled by the tendency of the element in question to adsorb or to remain in solution (dissolved load) and the ability of surface waters to remove and transport particles (adsorbed load). Results for the Swiss aquatic system on radionuclide speciation, particle erosion and transport illustrate the phenomena and help to quantify the migration processes.

The first example deals with liquid discharges from nuclear power plants and their behavior in the river sections downstream. ^{60}Co represents an ideal test case because of its known mobility [1] and its participation in most relevant biogeochemical aquatic processes. Data collected in various river and lake systems of Switzerland allow calibration of a model which combines codes developed for the physics of aquatic systems [3] with a metal speciation code [2]. In spite of the long list of parameters controlling the behavior of Co, critical single parameters, such as the concentration of organic ligands have been found to explain results collected in situ (Fig. 1).

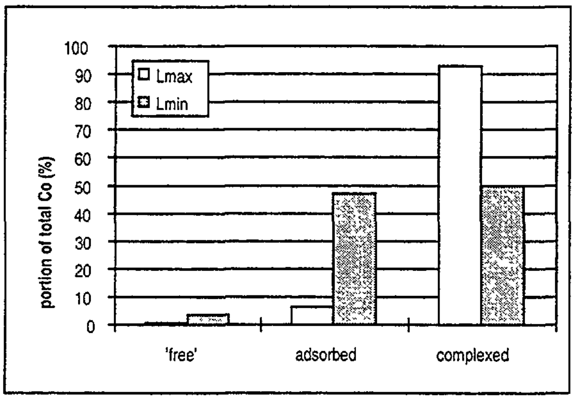

FIG. 1. Speciation of cobalt in the rivers Aare and Rhine below the Swiss nuclear power plants at pH 8; 'free' indicates the cationic form; adsorbed, the portion associated with suspended particles and complexed, the portion that reacted with natural organic ligands (Lmin = 1.4nM; Lmax = 7.6nM [4]). Both 'free' and complexed forms are more readily transported toward the oceans.

Fig.1 also shows that depending on ligand concentration the majority of Cobalt is organically complexed, which reduces its adsorption ability and explains its mobility. The second example illustrates the importance of erosion for the transport of strongly particle-reactive radionuclides like Plutonium and Cesium. Sediment cores from Swiss lakes indicate ^{137}Cs maxima related to atmospheric atomic bomb testing and the Chernobyl accident, but transport to the lakes continued after deposition as a result of erosion in the catchment area (FIG. 2). For ^{239}Pu a maximum of 2 Bq/kg is found in sediments from the 1960ies, but activities have remained at a relatively constant level of 0.2 Bq/kg in the 1970ies and 80ies, dropping in recent suspended matter to 0.1 Bq/kg. Quantification of erosion processes is still difficult, because they depend on external (weather pattern, agricultural activity) and internal (mineralogy and physics) parameters, which remain poorly defined. Based on data from Swiss lakes it is possible to estimate Cs and Pu removal for much larger catchment areas. Such erosion processes are of particular importance in contaminated areas.

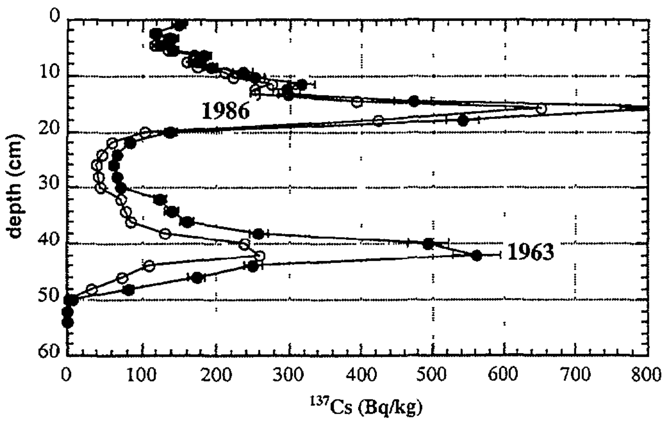

FIG. 2. Depth distribution of ^{137}Cs (decay-corrected to the date of sampling, 7.12.97, open circles and to the time of deposition, filled circles, with 2□ measurement error) in a sediment core from lake Greifen. The continued radionuclide flux from 1963 to 1986 and after 1986 is an indication of erosion in the catchment area.

On the basis of reports on liquid discharges from nuclear installations world wide, an estimate of the portion of radionuclides, which reach the oceans can be carried out using the Swiss test case as representative. Similarly, erosion estimates for Switzerland allow an assessment of the bomb and Chernobyl-related flux toward the oceans.

Acknowledgements

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XA9952005

CHEMOCLINE CHEMISTRY

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The chemocline is the borderline between the upper oxygen-containing (oxic) seawater and the sulfide-containing (anoxic) seawater below, i.e. the borderline between the living and dead sea.

The three most studied waters with more or less permanent chemoclines are the *Black Sea*, the Baltic Sea at the *Gotland Deep* and the Norwegian fjord *Framvaren*. All these three waters were created during the latest deglaciation some 8000 to 10000 years ago. Any change in the nutrient load or the meteorological and hydrological conditions will shift the depth of the chemocline and thus the living conditions for the marine life.

To be more specific: The hydrological conditions in the *Black Sea* can be changed by using the river water for irrigation which will shift the water balance. The density of the oxic layer will increase and the chemocline depth will decrease, i.e. move upwards.

In 1997 the summer in July and August was unusually warm in the Scandinavian area. Noxious algae blooms occurred, but the effect of the fallout in August-September on the *Gotland Deep* was not measurable with the analytical methods that were used.

Framvaren is connected with the North Sea through a man-made channel with a sill depth of 2-3 m. The chemocline at 20 m has been shifted downwards from 18 m in the last 15 years. It is tempting to deepen the channel in order to allow larger vessels into the fjord. This would lower the chemocline, but release hydrogen sulfide and kill off all fish in the oxic layer by asphyxiation.

All three areas are affected by river inflows and runoff. Besides the fresh water content of nutrients two river-borne species affect the systems: dissolved silica ($Si(OH)_4$) and iron (Fe^{2+} and $Fe(OH)_3$). The supply of silica is necessary for the spring blooms of siliceous algae and the fallout of biogenic opal. Iron is not only an essential trace metal but its availability is affected by the chemocline chemistry.

The most difficult part of the chemocline chemistry is the sulfur chemistry and microbiology. In the 3rd edition of Methods of Seawater Analysis [1] the chapters on the determination of hydrogen sulfide, sulfur and thiosulfate have been revised. In the future more attention is going to be given to elemental sulfur since it seems to be the key product of the reaction between oxygen and hydrogen sulfide and reaches its maximum concentration in the chemocline. Ralf Steudel has focussed the attention on the formation of polythionates [2] and devised methods for their determination [3]. Below the chemocline elemental sulfur is present as polysulfides ((H_2S_n).

The chemocline and the anoxic water below the chemocline affects many of the trace metals. The dissolved concentrations of the metals are determined by the solubility equilibrium, e.g. $MS(s) + H^+ \Leftrightarrow M^{2+} + HS^-$ (see ref. [4]) and the complex formation equilibrium $M^{2+} + 2HS^- \Leftrightarrow M(SH)_2$. A few reliable equilibrium constants have been obtained for iron(II) (6.45), zinc (12.9), cadmium(13.8) and mercury (37.7). As judged by the constants for mercaptoethanol ($HOCH_2CH_2SH$) in Table I the complexes MSH^+ may be neglected.

TABLE I. FORMATION CONSTANTS (log K_1) FOR METAL COMPLEXES WITH MERCAPTOETHANOL

Mn(II)	1.8	Cu(I)	16.7
Fe(II)	2.5	Ag(I)	13.4
Co(II)	(3.2)	CH_3Hg^+	15.9
Ni(II)	3.9	H^+	9.72
Cu(II)	8.1		
Zn(II)	5.7		
Cd(II)	6.1		
Hg(II)	20.0		
Pb(II)	6.6		

Only two beneficial properties may be connected with the chemocline: denitrification (elimination of ammonium and nitrate by formation of dinitrogen, N_2) and the elimination of a few toxic metals (e.g. cadmium and mercury) by coprecipitation with FeS and FeS_2.

The following equilibria and equilibrium constants explain the concentrations of iron below the chemocline in Framvaren at 20 m:

$Fe(s) + H^+ \Leftrightarrow Fe^{2+} + SH^-$; $\log K_s = -3.61 \pm 0.50$

$Fe^{2+} + SH^- \Leftrightarrow FeSH^+$; $\log K_1 = 2.6$

$Fe^{2+} + 2SH^- \Leftrightarrow Fe(SH)_2$; $\log K_1K_2 = 6.2$

The results for Framvaren and the Black Sea have been published in Aq. Geochem. 2(1996)111-129, 3(1998)329-343 and 3(1998) in print.

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VALIDATION OF A MARINE DISPERSION MODEL FOR THE CALCULATION OF DOSES TO THE EUROPEAN POPULATION

XA9952006

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A marine dispersion model has been developed at the National Radiological Protection Board (NRPB) to assess the radiological impact of radioactive discharges into the marine environment. The model is derived from the compartment model developed for the MARINA project [1] and forms part of the more general European Union methodology for assessing the radiological consequences of routine releases of radionuclides to the environment [2] . It describes the significant movements of radioactivity in European coastal waters. In the model, the different areas of the European marine system are represented by compartments and the movement of radioactivity between compartments is modelled using transfer rates. The regional marine model is interfaced with a local compartment model, usually represented by a single compartment, into which radioactive liquid effluents are assumed to be released. The local compartment describes the local environmental conditions, which may be very important in determining the impact of the radioactive waste. The transport processes considered in the model are: advection, diffusion and interaction with sediments. The adsorption of activity by sediments is due to both partitioning of the activity between the liquid phase and the solid phase (suspended sediments) and the removal of activity from the water column to bottom sediments. Both processes are modelled using element dependent distribution coefficients (k_d). The removal of activity from the water column is described by a panicle scavenging model. Each sea compartment has associated a seabed compartment divided into two layers. The removal of radioactivity is determined by distribution coefficients and by the rate of settling of the particulate matter. Movement between the two layers, burial in deep sediment, and the return of radioactivity to the water column through bioturbation and diffusion are also taken into account. The model predicts radionuclide concentrations in seawater, in suspended sediments and in seabed sediments. Concentrations of radionuclides in seafood are calculated from activity concentrations in seawater using equilibrium concentration factors. Activity concentrations in sand are related to the concentrations in the top layer of the seabed. The predicted radionuclide concentrations in marine materials are then used to calculate the intakes of these radionuclides by man through ingestion or inhalation, while activity concentrations in sediments are generally used to calculate intakes through inhalation of resuspended material or dose rates for external exposure. The NRPB marine dispersion model has been used in all the studies carried out at NRPB on the radiological consequences of releases into the sea. These studies include the assessment of the radiological exposure of the population of the European Community from radioactivity in the sea (MARINA and MAWNA-MED [3] projects) and the calculation of the present and future doses likely to be received by people living in the UK coastal region of the Irish Sea [4, 5].

A calibration of the marine dispersion models developed by Gfimwood [6] and Evans [7], on which the NRPB marine model is based, was carried out by Hallstadius et al. Activity concentrations of ^{137}Cs in the seawater of the North Sea, Skagerrak, Kattegat and Baltic Sea predicted by the models using historical discharges from Sellafield, Cap de la Hague and Dounreay were compared with measurements taken in the same areas. Transfer rates between compartments were adjusted to give the best fit between model predictions and actual observations. A validation of the Irish Sea section of the NRPB marine dispersion model was carried as part of the assessment of present and future doses to the population of the UK coastal region of the Irish Sea [4]. Activity concentrations of ^{137}Cs, Pu (alpha) and ^{241}Am in seawater and seaspray predicted by the model were compared with measurements taken by Ministry of Agriculture Fisheries and Food and United Kingdom Atomic Energy Agency in the Irish Sea.

The validation described in this paper focused on three radionuclides: Cs-^{137}, Tc-^{99} and Pu-$^{239.}$ Historical discharges of these three radionuclides from the main European nuclear installations, Sellafield, Cap de la Hague and Dounreay from the beginning of the operations up to 1995 were included in this study. Input into the North European water system as a result of fallout from nuclear weapons tests and the Chemobyl accident were also incorporated. Radionuclide concentrations predicted by the model in seawater, sediments and seafood up to 1995 were compared with measurements taken by different organisations in the waters of the European Continental Shelf and in the Arctic Ocean. Radionuclide concentrations calculated in various compartments were compared with average measurements taken in the same areas. The validation generally showed good agreement between the model predictions and the observations. Better results were obtained closer to the release point but no systematic over or under prediction by the model was found. A best fit analysis of the transfer rates was also carried out for all three radionuclides and the results of this exercise compared with the values currently used in the model.

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IAEA-SM-354/109P

INFORMATION MANAGEMENT SYSTEM FOR ENVIRONMENTAL PROTECTION IN THE COASTAL AREA OF JAPAN

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As a national level response to the International Convention on Oil Pollution Preparedness, Response and Co-operation, 1990 (OPRC 1990), Japanese Government established in 1995 a national system for responding promptly and effectively to oil pollution incidents. The system includes development of integrated information systems for oil pollution preparedness that should be prepared by related governmental bodies. In fiscal 1997, the Hydrographic Department (HO) has started to develop such an information system as an application of Geographical Information System (GIS).

Before the completion of the system construction, there happened one of the biggest oil spill incident around Japan; Nakhotka got a crash in the rough weather condition in the middle region of Japan Sea on January 2, 1997 and over 6240kl oil were spilt out from the vessel. Furthermore, on July 2, 1997, a tanker, whose name is DIAMONDGRACE, hit the sea bottom in the Tokyo bay and spilt out 1550kl oil. These incidents strongly allowed the government to realize the importance of practical system for oil pollution preparedness including information management for the coastal regions.

The system we have been developing aims to support oil spill response planning, assessment and responding activities. Maritime Safety Agency (MSA) which has primary responsibility for dealing with emergent situations at sea including oil spill incidents is supposed to be the primary user of the system. The system is designed to provide wide spectrum of information required in several stages regarding oil pollution incidents as geographically referenced information. It consists of an online data base which is accessible from all of our 11 regional headquarters, GIS softwares to prepare and present the required information and peripheral hardwares and softwares. The data base contains basic geographical data utilizing Electrical Navigation Chart (ENC), oceanographic data, socio-economic information related to oil pollution and information on disaster prevention (Fig.1).

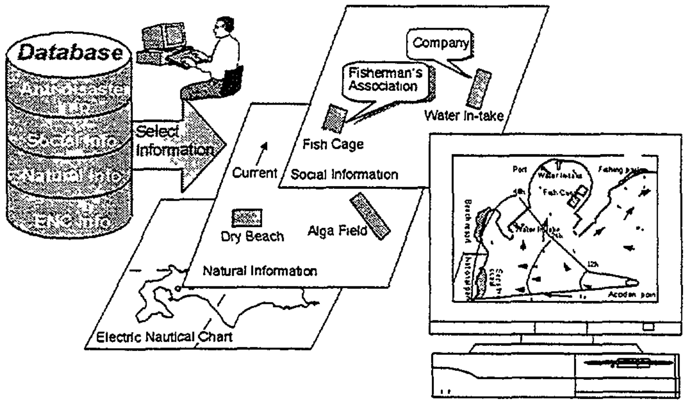


Fig. 1 System architecture of Information System for the Coastal Area

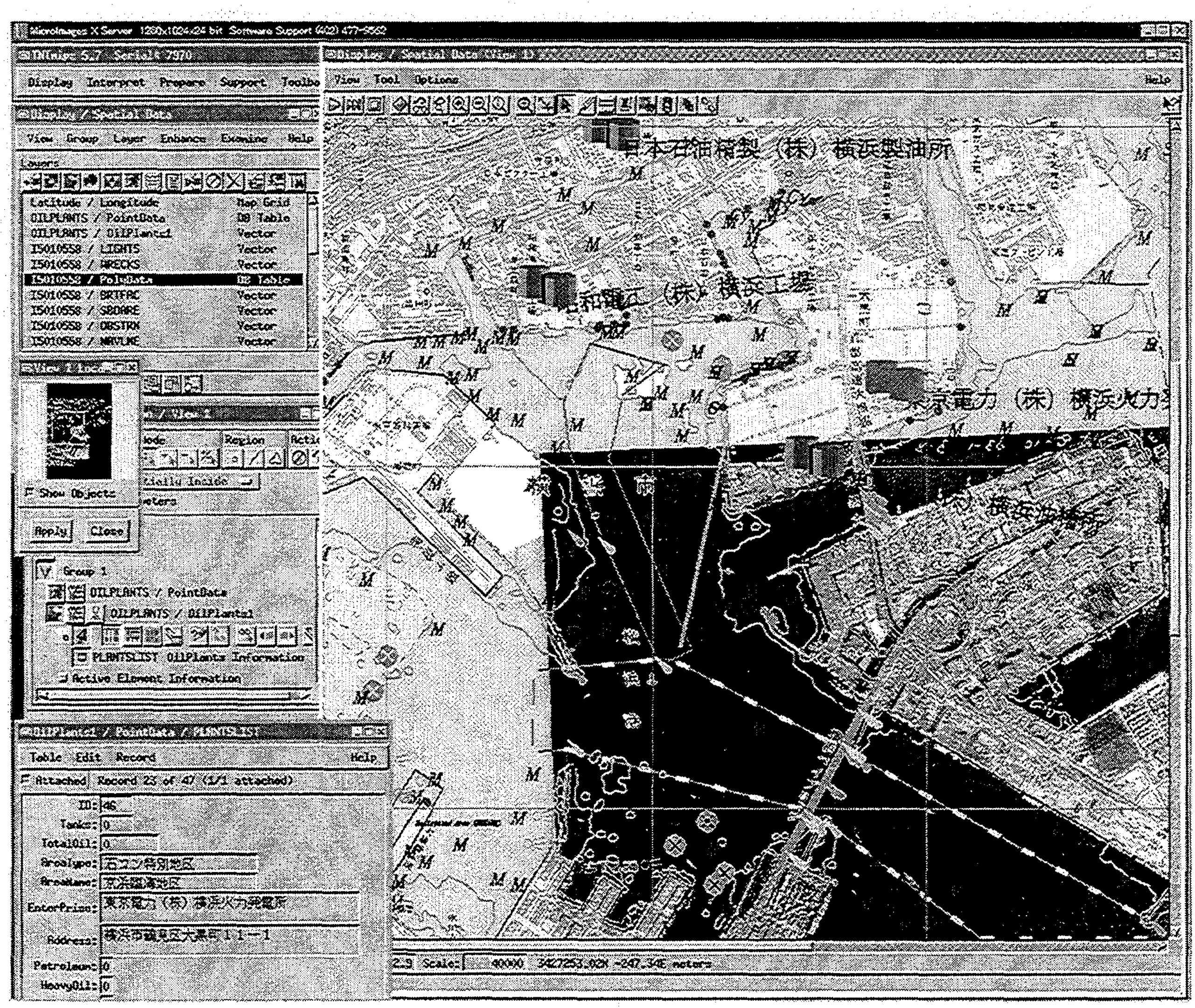
ENCs covering the area around Japan have been published by Hydrographic Department, MSA. ENCs are compiled in the S-57 format released by IHO. The S-57 is a concept for objective management of GIS to provide the standard to be used for the exchange of digital hydrographic data between national hydrographic offices and for its distribution to manufactures, mariners and other data users [1]. It is realized that our system is able to easily maintain the information on shore line types, which is important in clean-up activities for oil spill, because the system is based on ENC.[2] As for the oceanographic data of our system such as tides, tidal currents, waves and surface metrology, climate values of these are collected through Japan Oceanographic Data Center, and monitoring data are taken in our system through various way, for example, NEAR-GOOS (North East Asian Regional - GOOS, GOOS: Global Ocean Observing System) real time database operated by Meteorological Agency of Japan. As socio-economic information of our system, it includes fishery facilities, recreation sites, water intake facilities of life line etc.

And also, our system is designed to support some other functions; taking notes, scaling a distance and reproof, counting objects etc.

The presentation system is being constructed on a GIS software TNTmips that provides us with viewers for required information selected from the online database by overlaying multiple information layers.

Fig. 2 shows an example of the display of the coastal information which are under construction as applications of GIS. This system is able to show the attribute information of the symbol clicked by a pointer.

Fig. 3 shows the example for DIAMONDGRACE incident overlaying a satellite image of SPOT obtained by National Space Development Agency, Japan. We can understand the effectiveness of this system and satellite images.

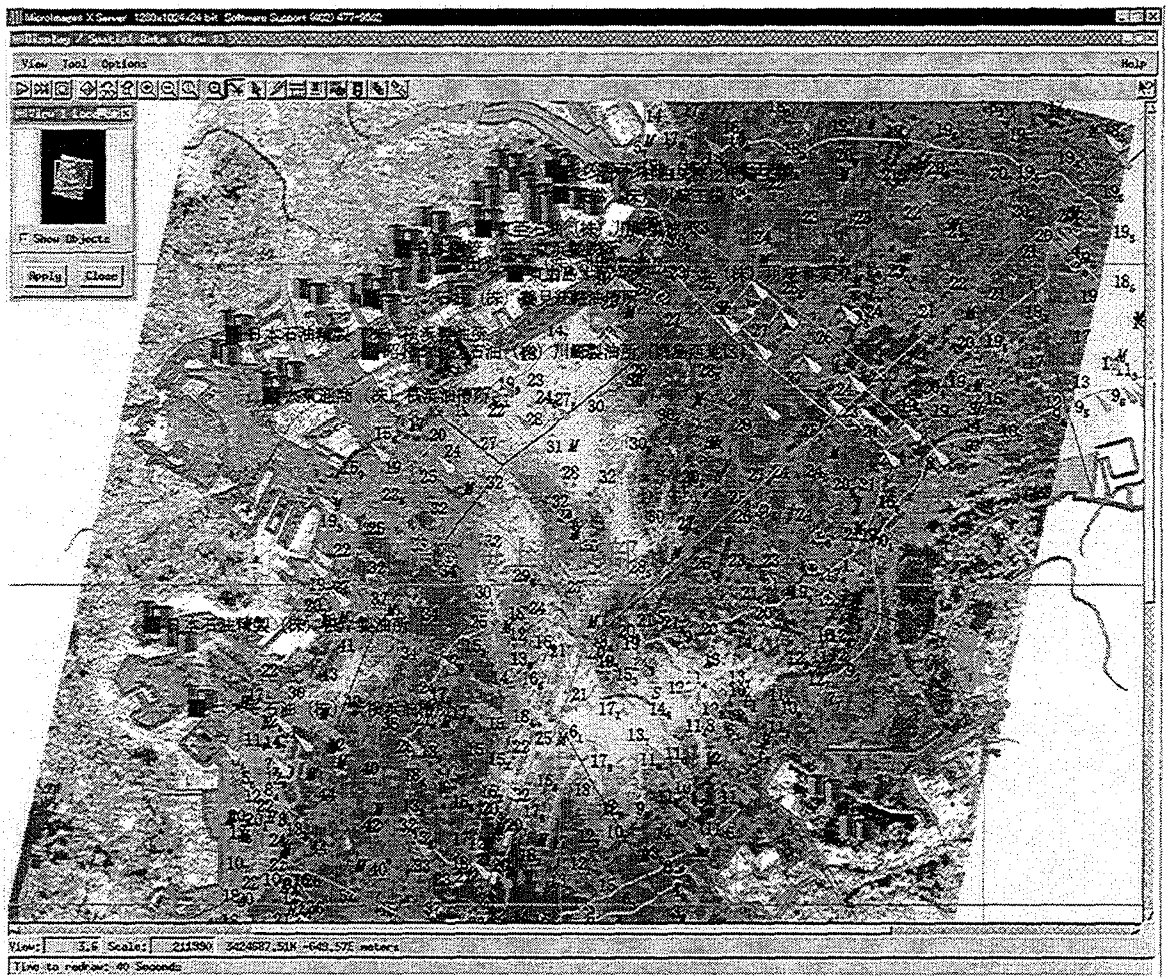


Latitude / Longitude	Map Grid
OILPLANTS / PointData	DB Table
OILPLANTS / OilPlants1	Vector
IS010558 / LIGHTS	Vector
IS010558 / WRECKS	Vector
IS010558 / PolyData	DB Table
IS010558 / BRTFAC	Vector
IS010558 / SBDARE	Vector
IS010558 / OBSTRN	Vector
IS010558 / NAVLNE	Vector

Attached Record 23 of 47 (1/1 attached)

ID: 46
Tanks: 0
TotalOil: 0
AreaType: 石コン特別地区
AreaName: 京浜臨海地区
EnterPrise: 東京電力（株）横浜火力発電所
Address: 横浜市鶴見区大黒町１１－１
Petroleum: 0
HeavyOil: 0

FIG. 2. Sample Display, Port of Yokohama of GIS system under construction at HD, MSA. This image overlays a land map, ENC information, aerial photo and oil storage facilities.



View: 3.6 Scale: 211390 3424587.51N -643.57E meters

Time to redraw: 40 Seconds

FIG. 3 Oil spill Accident in Tokyo Bay happened on July 2, 1997

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XA9952008

IAEA-SM-354/111P

A COMPARISON OF DOSES FROM ^{137}Cs AND ^{210}Po IN SURROUNDINGS OF NUCLEAR POWER PLANT JURAGUÁ DUE TO INGESTION OF MARINE FOOD

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Between 1991 and 1995 The Environmental Radiological Surveillance Laboratory of Cienfuegos carried out a Radiological Monitoring Program in the central area of Cuba, with the purpose of evaluation of the site of the first Nuclear Power Plant in construction in our country. As a part of this program natural and artificial background radionuclide levels in the marine environment were determined. From these results, two radionuclides caught our attention, ^{210} Po by his share to the internal irradiation dose and ^{137} Cs due to this possible increase when the plant operates.

The purpose of this work was the evaluation of the individual doses by ingestion of marine organisms in two residential areas with a great radiological interest: Cienfuegos city and Castillo de Jagua.

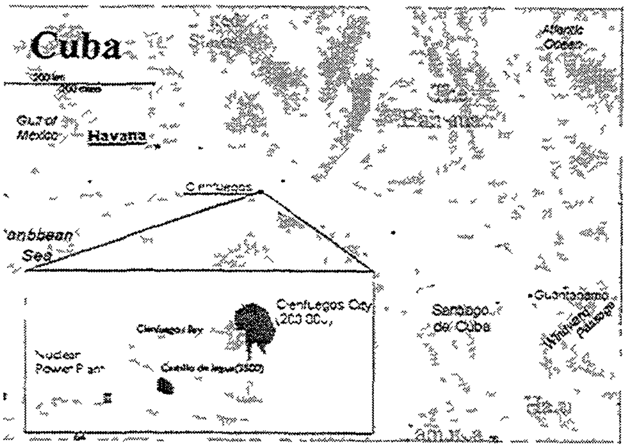

FIG. 1 Map of the studied areas.

Our work covered Cienfuegos City, the main residential focus of the province with an ingestion of marine organism near to the national average and the residential area of Castillo de Jagua, where is found a high ingestion rate because of his fishing habits.

The dose determinations were carried out from concentration levels in marine organisms edible parts, determined experimentally, and from the local ingestion rates in both areas. In our analysis were used the metabolic and Dosimetric models recommended by ICRP[1] .

Samples from 23 species of fish, mollusk and crustaceans were collected in Cienfuegos Fishing Port, taken to our Laboratory where the edible parts were separated and later analyzed. The ^{210} Po was determined by alpha radiometry after the spontaneous electrodeposition of the radionuclide in silver discs, from a clorhidric solution of the digested sample. [2] The ^{137} Cs analyses were carried out by gamma spectrometry in a system with a pure Ge detector and a passive lead shield after the radiochemical separation of the radionuclide.

Both essays are validated with OIEA reference materials and certified in compliance with ISO IEC-25.

The commercial network defined the Ingestion rate of Cienfuegos City, and the Statistic Province Direction and The Marine Products Distribution Company supplied the data.[3] In The Castillo de Jagua area was done a direct survey with a representative residential sample about their ingestion habits.

The concentration levels of ^{210} Po and ^{137} Cs are shown in Table No.1

The concentration levels of ^{210}Po in Cienfuegos Bay marine organisms are high in comparison with levels reported in literature [4]: 0.7 and 20 Bq/Kg in muscular tissues of fish and mollusk respectively. The ^{210}Po levels in the white shrimp reach values of 156 Bq/Kg.

The levels of ^{137}Cs are normal for a zone affected only by global fallout and are similar to other data observed by Baxter *et al* and Silva *et al* in 1987 for the Caribbean region. [5],[6]

In Castillo de Jagua the fish ingestion rate follows a lognormal distribution. The geometrical mean value was 51.1 Kg/year and the average 103 kg/year. The 95% percentile was 351 Kg/year and the representative interval from 21.4 to 116 Kg/year. The 1.6 % of population doesn't eat fish. The ingestion of mollusk and crustaceans is not significant.

TABLE I. CONCENTRATION LEVELS OF ^{210}Po AND ^{137}Cs.

Organism	**^{210}Po** Bq/Kg fresh weight	**^{137}Cs** Bq/kg fresh weight
Fish	19.5	0.1
	[5.2-89]	[0.09-0.3]
Mollusk	25	0.9
	[20-33]	[0.1-0.11]
Crustacean	125	0.1
	[50-156]	[0.06-0.2]

TABLE II. COMMITTED EFFECTIVE DOSES FOR BOTH POPULATION GROUPS.

	Ingestion Value Kg	Committed Effective Dose Po-210 (μSv)	Committed Effective Dose Cs-137 (μSv)
Cienfuegos	4.45	44.6	0.005
	51.1	516	0.06
Castillo de Jagua	351	3500	0.42
	21.4-116	200-1200	0.02-0.13

The fish ingestion rate in Cienfuegos City was 4.45 Kg/ year, similar to the national mean. The dose, according to all written above, takes into consideration only the fish ingestion.

In Table 2 are shown the doses for the two populations after all calculations including for The Castillo de Jagua area the 95% percentile value and the representative interval. The dose from ^{137}Cs is the 0.01 % of doses due to ^{210}Po. The 95% percentile in Castillo de Jagua reaches a dose of 3.5 mSv for ^{210}Po. This value is close to the ones reported for populations from the artic and subartic areas in north hemisphere which dietary habits are based on caribou and reindeer meat. [7] The Representative Interval dose is higher than the reported for the rest of the world due to food ingestion of 0.2 mSv. [4]

The mean individual dose from ^{137}Cs in seafood for Cienfuegos City corresponds to 12 minutes Effective dose of total food consumption for this population according to Suárez et al [8] (0.2 mSv per year) and 1 minute Effective dose from all natural sources (2.4 mSv per year)[4]. For The Castillo de Jagua population the geometrical mean dose from ^{210}Po corresponds to 251 days Effective dose of total food consumption for this population (0.7 mSv per year) [8] and 77 days Effective dose from all natural sources.

The ^{210}Po dose for The Castillo de Jagua population, due to its high ingestion rates and the slightly high levels of ^{210}Po, represents a significant contribution to the dose of total food consumption. It's necessary a further analysis about the possible sources of ^{210}Po in Cienfuegos Bay.

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XA9952009

DEGRADATION, RELEASE AND BIOAVAILABILITY OF DDT/DDE RESIDUES TO OYSTERS USING RADIOLABELLED TECHNIQUES

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The significance of residues in the sediment, in terms of bioavailability, both in their amounts and forms of uptake has been sparsely studied especially since this is the main route of transport of pesticides to the marine environment. This paper deals on degradation of sediment residues of DDT and DDE (extractable and bound), rate of formation of bound residues, release of sediment residues in hard *water, brackish water and synthetic seawater, its release in both sterile and non sterile brackish water and* the forms and amount released in the sediment and taken up by the oyster .

DDT was adsorbed readily in sediments equivalent to 94.98% of the added radioactivity of which 8.37% is desorbed in water and only 0.13% in seawater. Non extractable bound residues of DDT were formed in greater quantities in sediment/brackish water combination equivalent to 8.2% of initial concentration after 180 days in comparison to 0.8% in sand/synthetic water combination. Release of DDT from extractable sediment residues was observed in sterile and non sterile brackish water amounting to 0.046-0.086% of the radioactivity of the sediment. Likewise, non extractable bound DDT sediment residues were also released equivalent to 0.022% both in sterile and non sterile brackish water.

When ^{14}C DDT was added in an open microecosystem, DDT sank into the sediment with a half life of 2.9 days in brackish water. In a microecosystem composed of 800 g sediment (treated with 20 uCi ^{14}C DDT with specific activity of 12 mCi/mmole equivalent to 0.74 ug/g DDT), 9 liters water and 10 g fresh biota weight, DDT was detected in oyster with concentrations equivalent to 3.3, 9.4 and 3.9 ng/g in the fluids, muscle and shell, respectively after 30 days exposure. In mussel, the concentrations were 2.0, 8.0 and 3.6 ng/g respectively in fluids, mussel and shell after 30 days. For both mussel and oyster, 46-62% of DDT residues in biota were taken up by the shell, 19-31% in the muscle and 19-23% in the fluids.

In another uptake study composed of 13.2 ng/g ^{14}C DDT sediment residues (10.3 ng/g extractable and 2.9 ng/g bound residues), oyster tissues contained 11.4 ng/g and mussel 2.5 ng/g after 5 and 2 days exposure, respectively. All biota residues were in extractable form.

In another microecosytem study composed of 400 g sediment (treated with 8 uCi DDT equivalent to 0.59 ug/g and aged for three months), 15 liters brackish water and 25 g fresh biota weight, the initial DDT residue after aging was 0.154 ug/g (71.5% as extractable and 28.5% bound). The initial extractable residues were 90.7 % in the form of DDT. After 30 days the residues decreased to 0.129 ug/g with a decrease of both extractable and bound residues. However, extractable residues increased to 74.4% in relation to total sediment residues and 89.4% were in the form of DDT. Residues in the sediment were released into the water equivalent to 0.3 ng/ml (99.4% as DDT) with 0.4 ng/g residues in oyster tissues and 99% of biota residues were extractable. The extractable residues in biota were 54.4% DDT and 45.6%

DDE suggesting the transformation of DDT to DDE by the oyster either before or after it was absorbed.

Sediments containing ^{14}C DDT residues were exhaustively extracted with only bound residues *left and a microecosystem composed of 400 g sediments, 15 liters brackish water and 18 g fresh tissue* was set up. Initial bound residues were 22.5 ng/g and at 30 days after treatment, total sediment residues declined to 5.0 ng/g with 1.3 ng/g in extractable form (as DDT) and 3.7 ng/g as bound. This indicates the change of residues from bound to extractable form. Sediment residues were released into the water equivalent to 6.7 pcg/ml with total residues in oyster equivalent to 0.46 ng/g of which 0.22 ng/g extractable and 0.25 ng/g bound. The extractable residues in biota were 53.8% DDT and 46.2% DDE which again indicate transformation of DDT to DDE by oyster.

To study the uptake of DDE, a microecosystem composed of 1 kg sediment (treated with ^{14}C DDE with 1138.6 MBq/mmole and equivalent to 20 ng/g), 8 liters brackish water and 14 g fresh biota weight was set up. With an initial concentration of 17.73 ng/g total sediment residues (15.08 and 2.65 ng/g for extractable and bound residues respectively), 0.44 ng/g was detected in the water. In oyster tissues, 37.37-46.28 ng/g residues were detected as extractable and 18.99 ng/g as bound at 7-14 days after treatment. There was an increase of residues in fluids and increase in bound residues in tissues from 7 to 14 days after treatment and both DDE and DDD were detected in the extractable residue fraction of the oyster tissues.

In summary, sediment residues of DDT can be released in hardwater, seawater and in either sterile or non sterile brackish water from both extractable and bound residues. Released residues are mostly in the form of DDT and is taken up by both oysters and mussel and residues were detected in the shell, tissues and body fluids. Oysters were found to transform DDT to DDE and most biota residues were in extractable form.

XA9952010

IAEA-SM-354/118P

RIVER TRANSPORT OF RADIONUCLIDES TO THE ARCTIC SEAS, THE BALTIC SEA AND THE BLACK SEA

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The study "Cross-Border Environmental Problems Emanating from Defence-Related Installations and Activities" was initiated by the Norwegian Ministry of Foreign Affairs in 1992 and the project was established as a cooperation between the countries of the former Warsaw-pact and NATO within the North Atlantic Cooperation Council. One of the issues addressed in this study was: Radioactive Contamination of Rivers and Transport Through Rivers, Deltas and Estuaries to the Sea [1].

This subtopic focuses on the transport of radionuclides from different sources to the rivers and the transport via the rivers to the sea. The rivers and seas included in the study were: Ob, Yenisey, Lena and Mackenzie, Finnish rivers, Bug-Vistula, Danube, Dnieper and Colombia, and Arctic seas, Baltic Sea, Black Sea and the Pacific Ocean.

The deposition on the Kara Sea from global fallout was 0.9 PBq during the period 1962-1993 and 0.6 PBq on the Laptev Sea. The river transport with Ob and Yenisey rivers amounted to 1.4 PBq and with Lena river 0.5 PBq during this period. About 27% of the ^{90}Sr flux with Yenisey river water is estimated to be related to discharges from Krasnoyarsk MCIC. The ^{90}Sr discharge via Ob and Yenisey rivers to the Kara Sea and the ^{90}Sr flux with Lena to the Laptev Sea exceeds the direct deposition from global fallout on the sea surface of the Kara Sea and Laptev Sea, respectively. The total river transport to Arctic seas amounts to 0.5 PBq [2], and appear to be insignificant relative to other sources, but few data are available on particle transport of ^{137}Cs with Arctic rivers.

The deposition from global fallout on the Baltic Sea amounted to 1.8 PBq ^{137}Cs and 1.1 PBq ^{90}Sr and the river transport amounted to 0.070 PBq ^{137}Cs and 0.4 PBq ^{90}Sr prior to the Chernobyl accident [3,4]. The deposition on the Black Sea due to the Chernobyl accident was 4.5 PBq ^{137}Cs and 0.09 PBq ^{90}Sr. In the period 1986-1988 0.3 PBq ^{137}Cs was transferred to the Baltic Sea via rivers and particularly Finnish rivers [3,4]. The main river transport of ^{90}Sr occurred during the mid-1960s and represented almost 1/3 of the amount directly deposited from global fallout on the Baltic Sea surface. The river transport of ^{137}Cs prior to Chernobyl accounted for less than 1% of the amount deposited directly on the Baltic Sea, but increased to about 6% relative to Chernobyl fallout deposited on the sea surface. Large areas of Finland is water bodies and water saturated marshlands in which the mobility of caesium is high with resultant high transfer rates to the Finnish rivers.

The amounts deposited from global fallout on the Black Sea in the period 1960-1977 was 1.3 PBq ^{137}Cs and 0.65 PBq ^{90}Sr [5]. About 1.7-2.0 PBq ^{137}Cs was deposited directly due to the Chernobyl accident. For ^{90}Sr about 0.3-0.4 PBq was deposited on the Black Sea surface after the Chernobyl accident. The river transport with Danube was 0.005 PBq during the years 1986-1997 and 0.040-0.052

PBq ^{90}Sr, and with Dnieper 0.001 PBq ^{137}Cs and 0.063 TBq ^{90}Sr for the period 1986-1995 [6, 7, 8]. The river transport of ^{137}Cs to the Black Sea was negligible relative to fallout on the sea surface while the river transport of ^{90}Sr accounts for between 25-38% of the direct deposited amount from Chernobyl accident.

The river transport was found to be an important source of ^{90}Sr contamination for the Kara Sea, Laptev Sea, Baltic Sea and Black Sea, and for ^{137}Cs to the Baltic Sea.

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XA9952011

PREVENTING POLLUTION FROM US NAVY SHIPS

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In executing its military mission, the United States Navy is required to be “on station” for extended periods of time. The demands of a sustained military presence pose a serious dilemma in meeting international environmental mandates. On one hand, the Navy must conduct protracted peacetime operations in a relatively confined area in order to fulfill military needs in support of national interests. Yet, on the other hand, naval operations in that area may be constrained by requirements to refrain from disposing of solid waste in order to be in compliance with foreign laws and international treaties.

The US Navy is committed to protecting the marine environment consistent with its defense mission. Controlling solid waste disposal while at sea is a basic part of that commitment. US Navy ships pose significant solid waste challenges because of the high levels of manning and extended periods of deployment – an aircraft carrier will have over 5,000 personnel at sea for six months at a time.

The Navy has instituted a three-pronged approach to control solid waste disposal: 1) policies and procedures have been defined to provide clear guidance on responsibilities, 2) equipment has been installed to treat solid waste and 3) a proactive source reduction program has been established to minimize waste generation. While all three strategies are needed, it is widely accepted that maximum leverage occurs when waste can be avoided, in the first place, through source reduction.

The WRAPS (Waste Reduction Afloat Protects the Sea) Program is an outgrowth of the US Navy’s highly successful Plastics Removal in the Marine Environment (PRIME) Program. WRAPS extends the PRIME philosophy to all solid waste by examining every item that comes aboard US Navy ships for its solid waste impact. The objective of the WRAPS Program is to implement cost-effective products and procedures that: 1) reduce solid waste generation, 2) simplify waste management processes and 3) reduce manpower demands on shipboard personnel.

As shown in Table I, the program has conducted detailed surveys to characterize the components of the shipboard waste stream. Food, paper and cardboard constituted the majority of shipboard solid waste. The study teams also determined the sources of solid waste during the course of the survey, Table II. Each ship was divided into four sources: Food Service, Administration, Berthing and Other. By far, Food Service areas were the dominant generators of solid waste.

As a result of gaining this understanding about the nature of solid waste generated by warships, plans were developed under the WRAPS Program aimed at minimizing the sources of solid waste. This paper presents an overview of current WRAPS initiatives focusing on tactics that have been successful in advancing the overall pollution prevention strategy. For each initiative, project personnel have evaluated the precise effects on shipboard waste disposal.

Among the avenues that the US Navy is pursuing are:

- Increased reliance on reusable packaging for food will displace the many forms of single-use, disposable packaging that constitute a significant portion of ships' waste streams. Reusable plastic meat containers are being studied for their potential application to military food service operations.

- Reusable pallet-level, bulk containers would displace corrugated cardboard which is one of the single largest contributors to shipboard solid waste.
- Returning shop rags to shore for cleaning and reuse will eliminate the need for disposal of hazardous waste.
- "Junk mail" follows sailors like it does everybody else. Diverting unwanted mail would reduce paper waste.
- Providing technical manuals and other bulky documents in electronic form rather than paper also contributes to reductions in paper waste.

TABLE I. SUMMARY OF DISTRIBUTION CHARACTERISTICS FOR THREE SURVEYED SHIPS

	Weight		Volume	
Category	Percent	kg/person/day	Percent	lit/person/day
Food	50.39%	0.88	14.75%	2.61
Paper	17.87%	0.31	31.93%	5.60
Cardboard	14.67%	0.26	29.95%	5.26
Plastic	4.48%	0.08	12.24%	2.16
Textiles	3.18%	0.05	1.90%	0.34
Metal	6.56%	0.11	8.01%	1.40
Glass	1.63%	0.03	0.73%	0.11
Other	1.22%	0.02	0.49%	0.08
Total	100.00%	1.74	100.00%	17.56

TABLE II. SUMMARY OF SOURCE CHARACTERISTICS FOR THREE SHIPS

	FOOD SERVICE	ADMIN	BERTHING	OTHER	TOTAL
Weight (kg)	4253.09	297.57	285.78	768.9	5605.34
Percent	75.88%	5.30%	5.10%	13.72%	100%
kg/person/day	1.33	0.09	0.09	.24	1.75
Volume (liters)	35855.68	4825.91	4122.05	11573.17	56376.81
Percent	63.60%	8.56%	7.31%	20.53%	100%
lit/person/day	11.17	1.51	1.29	3.60	17.57

By adopting a proactive stance, the US Navy has made remarkable advances in reducing waste disposal from its ships at sea. In addition to satisfying environmental mandates, the US Navy has preserved shipboard quality of life while practicing responsible environmental stewardship.

XA9952012

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DISTRIBUTION OF SOME ORGANOCHLORIDE PESTICIDES IN THE ALL SAINTS BAY, BAHIA, BRAZIL

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First restrictions to organochlorine insecticides (OC) in Brazil date of 1976 and by 1985 they were completely prohibited However use of existing stocks and smuggled parcels as well as official use in malaria campaigns still takes place. During the SH summer of 1995 a cross- sectional survey was conducted for organochloride pesticides in 12 intertidal sites, both in sediments and in some selected edible species of the All Saints Bay, east of Brazil. Samples were collected during low tide, except for the fishes which were obtained from local fishermen. Individuals of medium size were selected in the field for each bivalve species and for crab, which later were pooled together by species and station for storage - 18°C until analysis Composite samples were obtained from portions of intertidal sediments randomly obtained %from a grating. Detergent washed and water, acetone and dichloromethane rinsed tools and glassware were used at all times. Subsamples of sediment placed in precleaned thimbles were extracted in Soxhlet for 24h with dichloromethane and methanol (2:1) containing activated Cu wire and those of fauna were extracted with three potions of dichloromethane for 5 min using ultrasound, followed by clean-up on 5% water deactivated silica-alumina (Cu powder added in case of sediments). Organochloride determinations were accomplished by injecting luL of the proper fractions diluted in iso-octane into a GC/^{63}Ni electron capture detector (Varian Star 3400), using a 30m, 0.25mm DG-5 column and He as carrier gas. Detection was 2,5 pg/uL and limit of quantification for an average 8g sample diluted to lmL was 0.25 ng/g. Accuracy was determined by analysis of the IAEA 140 seaplant homogenate sample, with obtained results for each DC lying within the acceptable range.

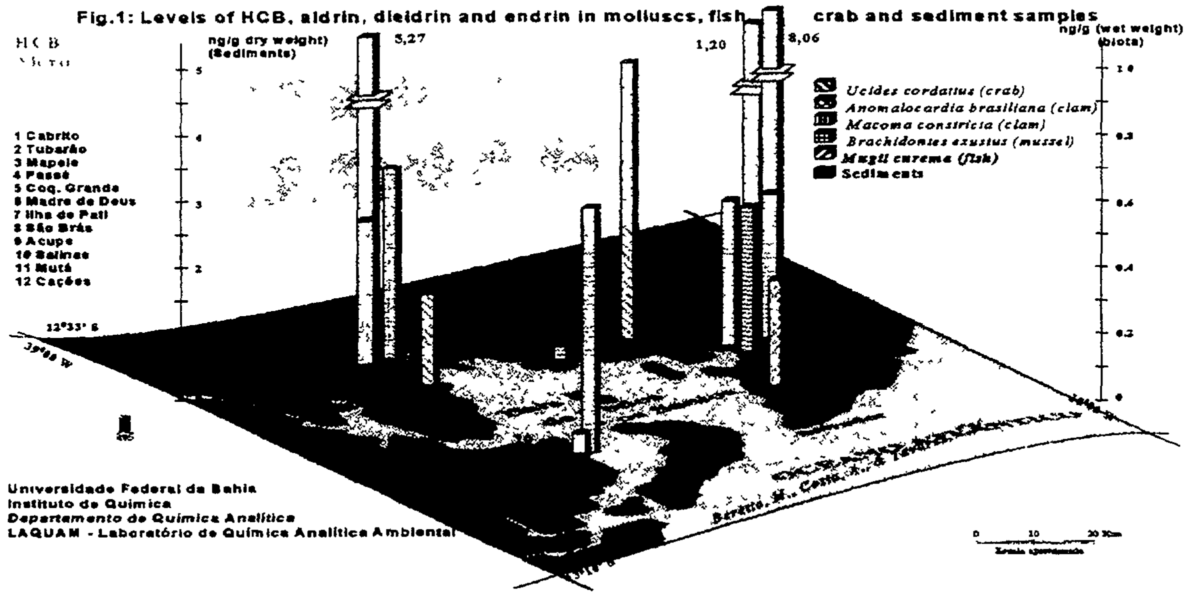

FIG. 1. Levels of HCB, aldrin, dieldrin and endrin in molluscs, fish, crab and sediment samples.

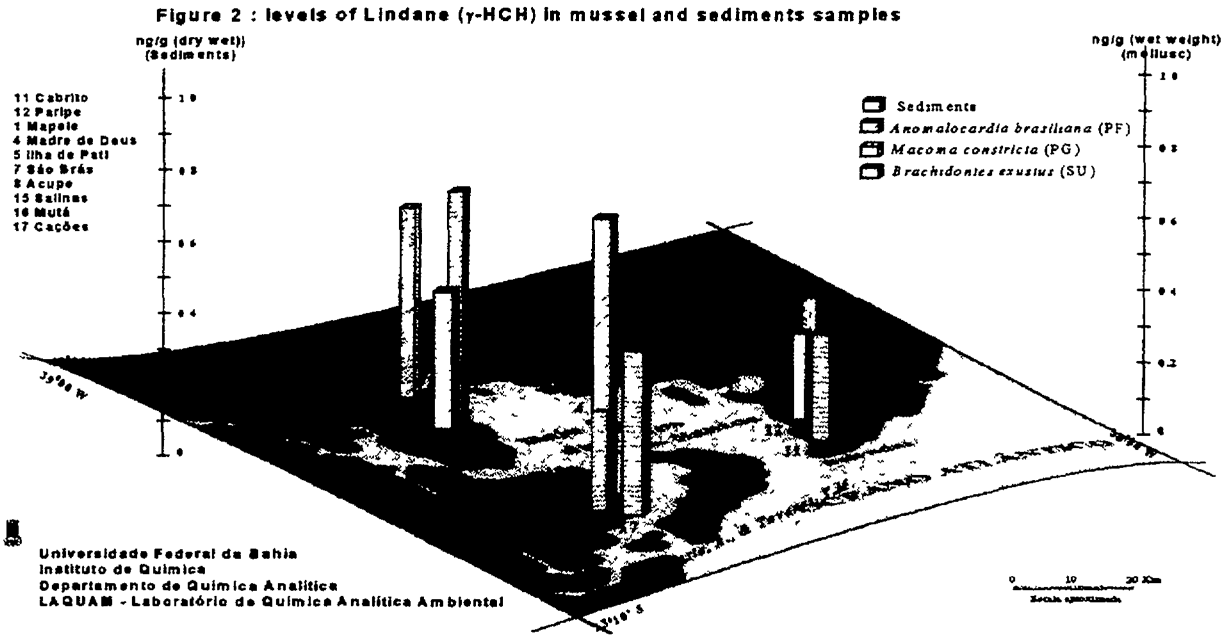

FIG. 2. levels of Lindane (γ-HCH) in mussel and sediment samples.

Lindane has been found in several sites in sediments and in all fauna species, by levels were always below 1.0 ng/g. Fig. 1 display the results. HCB, Aldrin, Diedrin and Endrin were found in several of the studied sites, both in sediments and in the different fauna species, with higher results found in the E and NW of the bay. Distribution and levels can be seen in Fig. 2.

Highest level in sediments was 8ng/g dry weight and for fauna was 5 3ng/g wet weight in mussel (Brachidontes exustus) found in Mapele, at the E of the bay, where sources are unknown, since this is a highly industrialised area, and no production of OC exists

IAEA-SM-354/123P

MANGANESE KINETICS IN THE SHORE CRAB *CARCINUS MAENAS* EXPOSED VIA FOOD AND WATER

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Oxygen depletion in marine water has been an increasing problem in many coastal areas due to eutrophication (Rosenberg *et al.*, Ambio 19, 102, 1990). Under hypoxic and anoxic conditions in bottom waters, the flux of manganese out of the sediment increases and substantial concentrations of dissolved manganese in the water column can be reached. Manganese liberated as Mn^{++} from the sediment during hypoxic conditions is re-oxidised fairly slowly (in order of weeks) after reintroduction of oxygen to the water (Dehairs et al. Est. Coast. Shelf Sci. 29, 457, 1989). Therefore, benthic organisms may encounter concurrent exposure to increased manganese concentrations and hypoxic condition.

Only few investigations have been carried out on the kinetics of manganese in benthic organisms and the purpose of the present was to investigate manganese kinetics in the shore crab *C. maenas* and the effect of hypoxia on manganese accumulation.

Exposure via food. To obtain a homogenous source of food, soft parts of blue mussels *Mytilus edulis* were homogenised in a food processor and ^{54}Mn was added. Gelatine was added and food blocks were made as described by Hansen & Bjerregaard (Mar. Pollut. Bull. 31, 127,1995). Crabs received one labelled meal every second or third day.

Exposure via water. Crabs were exposed to either ^{54}Mn or unlabelled Mn in glass or polystyrene aquaria at ca. 14.5 EC and 15 to 22 l and a 12:12 light:dark regime. In the hypoxia experiment, oxygen saturation was adjusted by means of a GM-602 gasmixer and the oxygen concentration was controlled daily by a PHM73 oxygen meter (Radiometer).

Manganese determination. Whole body counts for ^{54}Mn were obtained by means of a Bicron well-type NaI(Tl) crystal with a diameter and depth of 7.6 cm; ^{54}Mn in tissue and water samples were determined on a 1480 Wizard^{TM} 3". Stable manganese was measured by ordinary flame AAS.

Crabs exposed to ^{54}Mn in the water accumulated manganese almost linearly with time to whole body CF=s of 20 after 22 days. Manganese was eliminated according to 1. order kinetics with a half life of 44 days. The exoskeleton contained the major part of the manganese taken up from water.

Crabs fed ^{54}Mn containing food assimilated between 22 and 51 % of the ^{54}Mn ingested. The crabs reached a steady state concentration after approximately one week. Manganese taken up from food was lost according to 1. order kinetics with a half life of 96 days.

Manganese concentrations in unexposed crabs were approximately 2-3 Fg Mn g^{-1} wet weight in midgut gland and muscle, 3 in gills, 1 in testes, 2 in hypodermis and 100 in carapace. No significant (ANOVA) amounts of non-radioactive manganese was accumulated in the tissues over 35 days from 50

Fg Mn l^{-1}. Exposure to 300 Fg Mn l^{-1} over 14 days led to increased concentrations in hypodermis (p=0.013) and muscle (p=0.039); no other tissues were affected. In some of the tissues a fairly high variability in manganese concentration was seen in the groups sampled weekly. The variability was mainly due to single, high values.

In another experiment groups of ten crabs were exposed to 0, 2, 2, 4 and 8 mg Mn l^{-1} for 7.5 days at either 100 % or 19 % oxygen saturation. Exposure to 2 and 2 mg Mn l^{-1} led to an almost linear increase in manganese concentrations in the tissues analysed (gills, midgut gland and carapace) whereas exposure to 4 and 8 mg Mn l^{-1} caused no or little further accumulation. Two-way ANOVA analysis demonstrated that hypoxic conditions augmented accumulation of manganese in midgut gland (p=0.001) and lowered accumulation in carapace (p=0.039), whereas the accumulation in gills was not affected by the oxygen tension.

^{54}Mn kinetics in *C. maenas* is very similar to the kinetics found in another benthic invertebrate, the sea star *Asterias rubens* (Hansen & Bjerregaard, Mar. Pollut. Bull. 31, 127,1995).

It is noteworthy that the potential for manganese accumulation predicted from the studies with the radioactive isotope is not reflected in actual accumulation in crabs exposed to stable manganese.

Although there was a significant effect of hypoxia on manganese accumulation in midgut gland and carapace, the effect was only moderate. *C. maenas* increases ventilation during hypoxia (Taylor, J. exp. Biol. 65, 309, 1976). This might result in increased uptake into the organism (including midgut gland), but the effect would have been expected to be reflected in the gills also, which is not the case. The mechanism for the effect of hypoxia on manganese accumulation in the carapace (probably mainly adsorption) cannot be explained; however, the adsorptive properties of the carapace of *C. maenas* seem to be affected by the general physiological status of the organism (Bjerregaard, Aquat. Toxicol. 2, 113, 1982).

XA9952014

IAEA-SM-354/124P

COMPARATIVE BIOACCUMULATION AND TOXICITY OF SILVER IN DIFFERENT POPULATIONS OF THE INTRA-SEDIMENTARY CLAM *MACOMA BALTHICA* EXPOSED OR NOT TO METAL CONTAMINATION IN THEIR NATURAL MEDIUM

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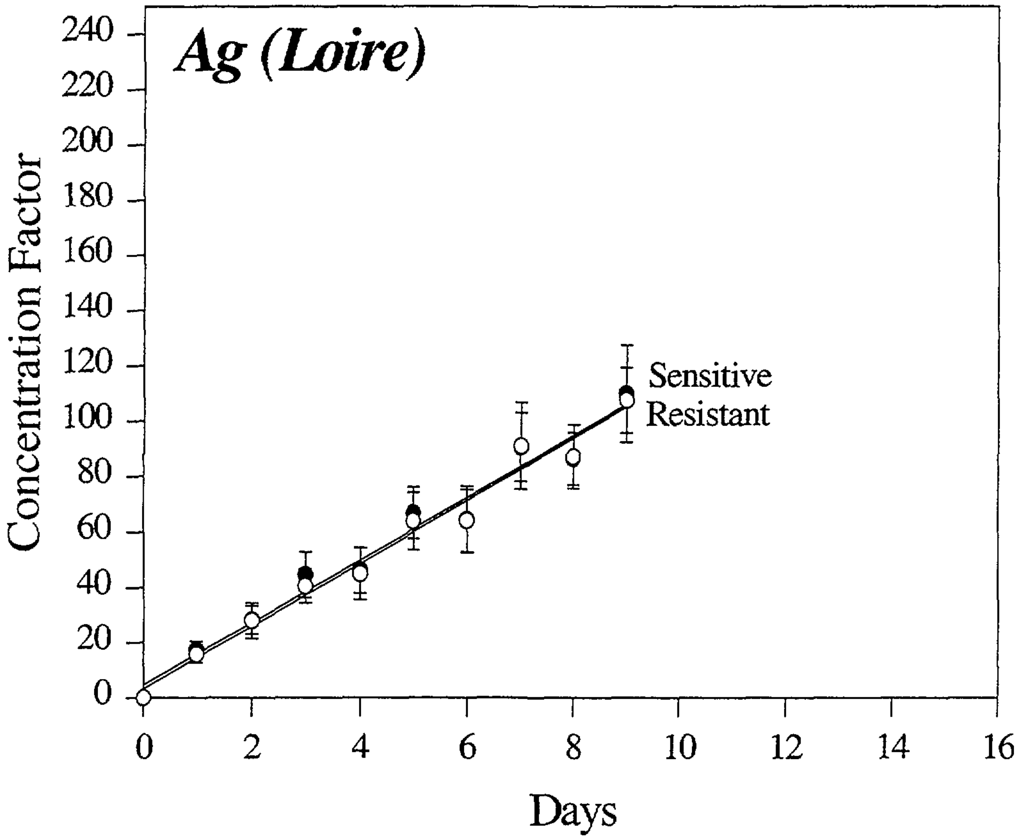
Tolerance to pollutants was observed in living organisms chronically exposed in their environment [1] and detoxification processes have been evoked to explain such observations [2]. In the present study, this hypothesis has been tested in clams originating from an industrialized estuary (Loire, Fr) and from an area submitted only to low anthropogenic influx (Bay of Somme, Fr). The comparison was carried out at different contamination levels in clams exposed to silver (50 to 100 ng $Ag.ml^{-1}$ till LT 50 when 50 % lethality was reached), a metal which has been described as liable to be detoxified through insolubilization and/or binding to metallothionein (MT).

The hypothesis of increased resistance in populations originating from polluted areas was not confirmed in the present study since lethal effects as well as cytological disturbances due to Ag were not clearly different in *M. balthica* from the Loire estuary and from the Bay of Somme. The physiological status, as reflected by the condition index, appeared as a relevant component of resistance, irrespective of the site. The use of a radiotracer (^{110m}Ag) concurrently with sublethal doses of stable Ag allowed us to know the bioaccumulation potential of sensitive (dead during exposure) or resistant clams (survivors). For both geographical sites, survivors did not protect themselves against metal toxicity by accumulating a significantly lesser amount of Ag than clams which did not survive metal stress (see figure for the Loire estuary). Moreover, survivors showed similar Ag levels in their soft tissues as well as a similar distribution between cytosol and insoluble ligands, the latter being the major sink. In some individuals, silver was sequestered in small granules located in basement membranes of the digestive gland but such ultrastructural figures were absent in other individuals. The distribution of cytosolic silver by using gel permeation as also shown individual differences. In different clams, Ag-ligands were mainly compounds showing molecular weight consistent with MTs or high molecular weight compounds. However, MT-like protein (MTLP) levels, similar at both sites, were not modified in contaminated clams suggesting that this protein was not induced in *M. balthica* by exposure to Ag. Nevertheless, survival was not only a short term resistance since cytological effects were moderate in view of acute doses used in experimental exposures. Thus, tolerance could be due not only to specific detoxication processes but also to more general physiological processes suggested by the relationship between survival and high condition indexes.

The specific variability was observed in different bivalves exposed to Ag [3]. In the case of *M. balthica*, important individual (this study) and inter-population variabilities are added to this specific variability, such as the presence [4] or the absence [5] of MTLP. Concerning the Loire estuary and the Bay of Somme, the tolerance due to environmental pressure could be envisaged as a consequence of acclimation to chronic pollution, the hypothesis here-tested. An alternative hypothesis was that in the Loire estuary, close to the southern limit of distribution of *M. balthica*, clams did not profit by optimal natural conditions, leading to a higher sensitivity to any additionnal stress, including metal exposure [6].

In conclusion, these results re-inforced the recommandation by [1]: "It seems dangerous to relax water quality criteria on the assumption that all populations in polluted environments will evolve an increased resistance".



Acknowledgements

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IAEA-SM-354/125P

BIOAVAILABILITY OF PARTICLES AND LOW MOLECULAR MASS SPECIES TO THE MUSSEL *MYTILUS EDULIS*

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To study the bioavailability of metals associated with suspended sediment fractions, the "pulse chase" method described by [1] has been used with mussels in biotest experiments. Sediments from the Stepovogo fjord on the east coast of Novaya Zemlya were spiked with very low concentrations of the γ-emitting nuclides ^{134}Cs, ^{60}Co, ^{65}Zn and ^{109}Cd. The spiked sediments (< 20 μm) were diluted in seawater (to about 6 μg/l) and fed to the common blue mussel (*Mytilus edulis*). Seawater and mussels were collected at the marine biological station in Drøbak on the Oslo Fjord, Norway. Similarly, blue mussels were also exposed to spiked ultra-filtered (< 3 kDa) seawater and thereby exposed to low molecular mass (LMM) species. The use of γ-emitting nuclides makes it possible to follow the temporal metal concentration in each mussel in a non destructive manner, thereby significantly reducing the biological variability. Based on measurements of individual mussels, retention curves were obtained (Figs. 1 and 2).

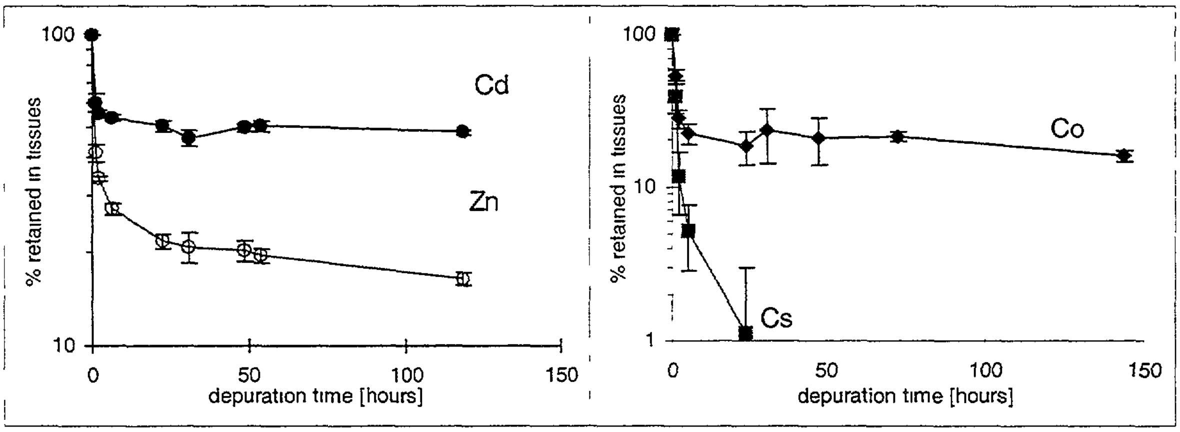

FIG. 1. Retained particle associated trace metals in the mussels as a function of time after ingestion of radiolabeled sediment particles (n = 3-5, ± 1 SD). The amount that is still retained after 72 hours of depuration is assumed to be assimilated. Note that the logarithmic vertical axes do not have the same scale.

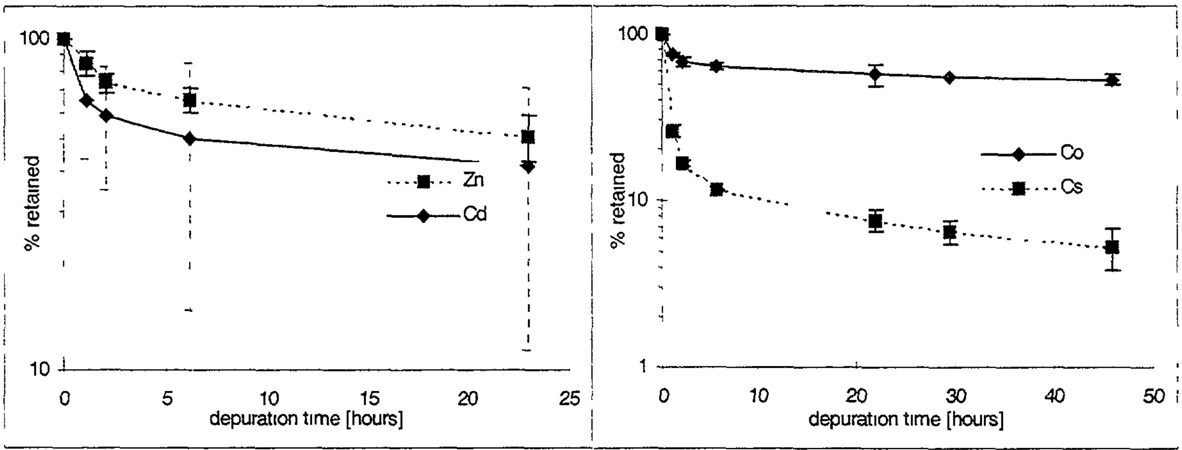

FIG. 2. Retained LMM trace metal species in the mussels as a function of time after exposure to tracer diluted into ultra-filtrated (<3 kDa) seawater (n = 2-4, ± 1 SD). Note that the logarithmic vertical axes do not have the same scale.

At the end of each experiment, the mussels were dissected. The results demonstrate that particle associated metals were preferentially associated with the mussel soft parts (Cs not detected), and that LMM Zn and Co were preferentially associated to the shell, while the LMM Cd and Cs were preferentially found within the mussel soft parts.

The assimilation efficiency coefficients (AE) were estimated using compartmental modelling (Fig. 3). The mussels were divided into two compartments describing an initial fast egestion and a subsequent slower physiological turnover.

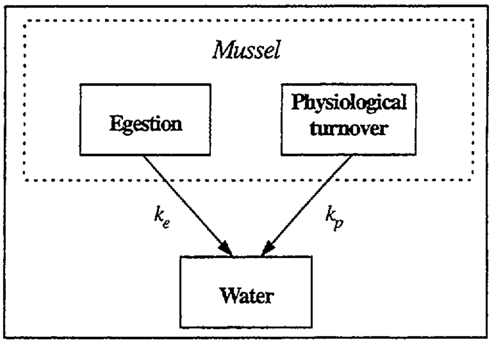

FIG. 3. Compartment model describing the depuration of metals ingested by mussels.

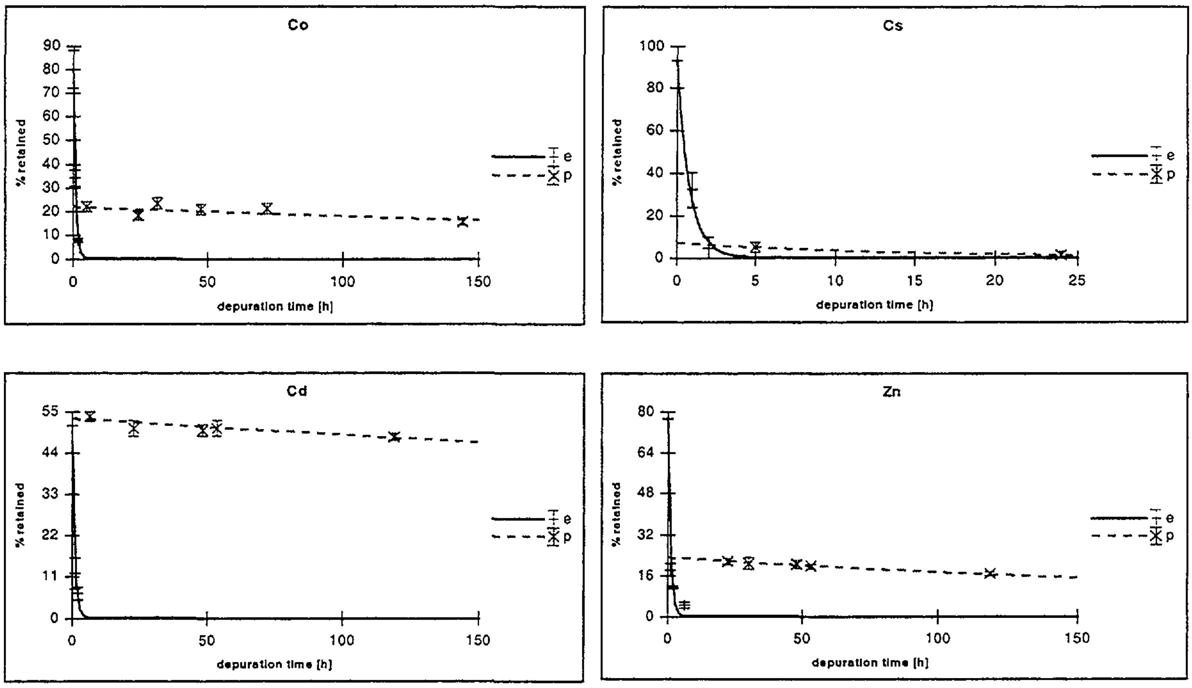

FIG. 4. Best fit curves achieved by the numerical optimisation program ModelMaker (Cherwell Scientific).e = egestion and p = physiological turnover.

By fitting the model parameters to the experimental data using numerical optimisation (Fig. 4), the biological half lives ($t_{b1/2}$) of the two compartments and the assimilation efficiency (AE) were estimated (Table 1).

For filtering organisms, like blue mussels, the initial uptake of particle associated metals is significantly higher than for LMM species. Furthermore, AE's estimated for LMM species are significantly lower than for particle associated trace metals.

TABLE I. BIOLOGICAL HALF-LIVES FOR THE TWO COMPARTMENTS, AND ASSIMILATION EFFICIENCY FOR THE SPIKED SEDIMENT OBTAINED BY COMPARTMENTAL MODELLING.

	Ingested metal			
	Co	**Cs**	**Cd**	**Zn**
$t_{b1/2}$(e) [h]	0.62	0.56	0.71	0.75
$t_{b1/2}$(p) [h]	357	9.8	831	243
AE [%]	22	5	54	22

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IAEA-SM-354/126P

CONCENTRATION DES METAUX LOURDS CHEZ LA PALOURDE *Ruditapes decussatus (L.)* D'UN MILIEU LAGUNAIRE : LE LAC MELLAH (EL KALA) / ALGERIE

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Les teneurs en Hg, Pb, Cd, Cu et Zn ont été mesurées chez la palourde *Ruditapes decussatus(L.)* provenant d'un milieu lagunaire saumâtre situé à l'Est de la côte algérienne (El-Kala).L'étude a porté sur un total de 280 individus récoltés avec un pas d'échantillonnage saisonnier dans deux stations du lac au cours d'un suivi annuel de mars 1993 à mars 1994.La station I est située au sein d'un herbier à *Ruppia maritima* dans la partie nord-est du lac. La station II, au sud de la station I, est plus abritée que cette dernière.Les dosages sont réalisés par un spectrophotomètre d'absorption atomique équipé d'un four à graphite, une flamme air/acétylène et un système d'hydrures pour la détermination du mercure total. L'analyse de ces éléments métalliques dans cette matrice biologique a révélé une différence de concentration, d'une part entre les saisons et d'autre part entre les deux stations. Cependant, le niveau de contamination en ces polluants est très faible.*Mots-Clés : Traces metals, molluscs, lagoons, pollution*

Les travaux relatifs à l'accumulation des métaux lourds à l'état de traces chez les mollusques et particulièrement chez la palourde en Algérie sont très peu nombreux et sont réalisés généralement de manière occasionnelle.

Dans le cadre d'une étude pluridisciplinaire, la palourde *Ruditapes decussatus* a été choisie pour diagnostiquer l'état de contamination par les métaux traces (zinc, cuivre, plomb, cadmium et mercure) d'un milieu lagunaire. Ce travail a été réalisé dans un site lagunaire saumâtre, le lac Mellah. Celui-ci est le siège d'une importante activité de pêche (mulets, soles, loups, anguilles), et d'essais de conchyliculture (moules, palourdes). Un contrôle sur les variations des concentrations en métaux traces chez la palourde *Ruditapes decussatus* a été entrepris, conformément à la recommandation du PNUE (Programme des Nations Unies pour l'Environnement) et du programme " MUSSEL WATCH " [1].

Dans cette étude, nous présentons les résultats acquis au cours d'un suivi saisonnier allant de mars 1993 à mars 1994 dans deux stations du lac.

Le lac Mellah est un lac côtier situé à l'est de l'Algérie (frontière algéro - tunisienne) dans la région d'El Kala (36°53'50" N, 8°19'30" E); de forme ovoïde, il occupe une superficie de 865 hectares. Il s'étend du nord au sud sur une longueur de 5 km et une largeur est - ouest de 2,6 km. Sa profondeur est généralement faible et atteint un maximum d'environ 6 m dans sa partie centrale.

Il est relié à la mer par un chenal de 900 m de long et 20 à 40 m de large (Fig. 1). Ce chenal est le siège d'échanges importants entre les deux milieux. Ces échanges influent intensément sur le renouvellement des eaux du lac et sont en partie responsables de son caractère saumâtre (30 p.s.u.) [2].

La lagune subit aussi l'influence simultanée de trois oueds : oued El Rekeibet, oued El Mellah et oued El Aroug ; ce dernier est relié au lac par l'intermédiaire d'un marécage. L'influence de ces oueds qui traversent des zones cultivées se traduit par des apports telluriques et hydriques importants surtout en période hivernale.

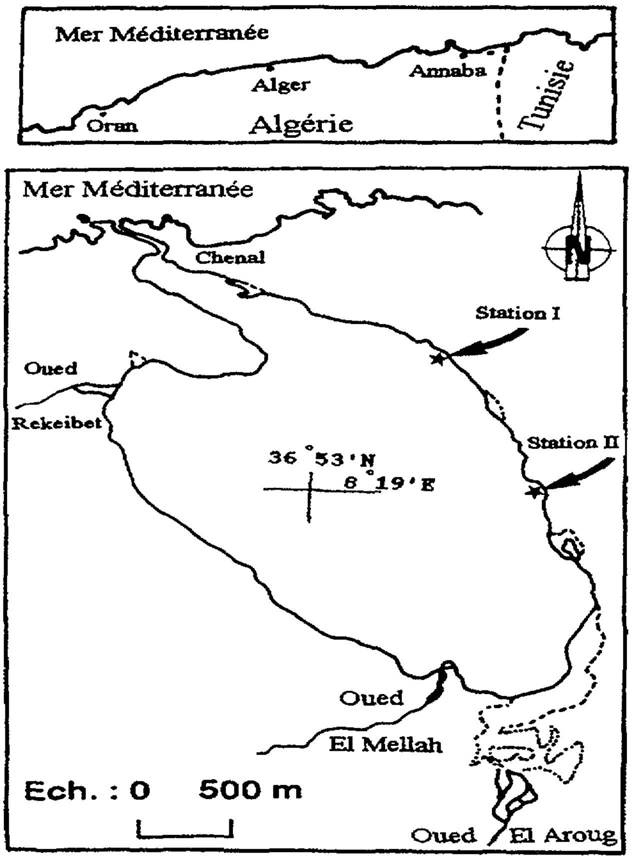

FIG. 1: Carte du site d'étude et localisation des stations

Les échantillons de palourdes ont été récoltés au niveau de deux stations (Fig. 1) : la station I est située au sein d'un herbier à *Ruppia maritima* à 0.55 m de profondeur. La station II, au sud de la station I et plus abritée que cette dernière, est située dans un champ de roseaux (0.65 m de profondeur), dans un rayon ne dépassant pas 20 m et dominé par un fond de sable fin. Les prélèvements ont été étalés sur un cycle annuel, avec un pas d'échantillonnage saisonnier. Une seule classe de taille a été retenue : [2.5 à 4.5] cm; soit une taille moyenne de 2.96 cm ±1.96. Dans chaque prélèvement, une trentaine d'individus a été récoltée. Les échantillons sont débarrassés de leurs coquilles, lyophilisés et micro-pulvérisés [3], puis minéralisés à l'aide d'acide nitrique ultra-pur (70 %, RIDEL DEHAëN).

La validité des résultats obtenus a été testée par la mise en œuvre d'exercices d'intercalibration sur des échantillons standards d'une matrice biologique fournis par l'AIEA (Agence Internationale de l'Energie Atomique) de Monaco, codés TUNA 351.

Les dosages sont réalisés d'après les méthode de UNEP [4] par un spectrophotomètre d'absorption atomique PERKIN ELMER 2380, équipé d'un four à graphite HGA 500, une flamme air / acétylène et un système d'hydrures MHS 10.

Les niveaux de concentrations des métaux lourds mesurés dans la chair totale des palourdes figurent dans le Tableau I. Les concentrations obtenues pour l'ensemble des métaux recherchés ne présentent pas, en général, de valeurs élevées. Leur ordre d'importance est en bon accord avec la littérature internationale concernant la consommation de ce mollusque. Les teneurs mesurées restent très faibles par rapport aux valeurs trouvées par EGEMEN *et al.* [5] chez *Tapes decussatus* de la baie d'Izmir (Turquie) et par BOUDJELLAL *et al.* [6] chez la moule *Mytilus galloprovincialis* du même site. Le zinc présente les concentrations les plus fortes par rapport à tous les métaux analysés.

TABLEAU I. CONCENTRATIONS MOYENNES DES METAUX TRACES CHEZ *RUDITAPES DECUSSATUS* DANS DEUX STATIONS DU LAC MELLAH (µg/g - P.S.)

		Zn	Cu	Pb	Cd	Hg
STATION I	**Min.**	6.50	1.8	0.70	0.09	0.020
	Max.	22.30	4.5	1.5	0.35	0.065
	M.	10.50	2.6	0.92	0.17	0.033
	SD	7.45	1.7	0.44	0.15	0.017
STATION II	**Min.**	5.7	2.1	0.6	0.07	0.0017
	Max.	19.8	3.8	2.0	0.27	0.055
	M.	6.7	2.5	0.55	0.11	0.030
	SD	7.5	1.6	0.50	0.30	0.018
	MG	11.4	2.9	0.82	0.09	0.042
	SD	6.5	2.0	0.75	0.17	0.017

Min. (Minimum). Max. (Maximum). M. (Moyenne). MG. (Moyenne Générale). SD (Ecart type).

Certaines teneurs détectées (Cd et Hg) sont à la limite de détection de la méthode d'analyse appliquée. Cependant, une légère variation saisonnière et entre les deux stations est à signaler pour certains éléments métalliques analysés (Fig. 2), due essentiellement à l'activité agricole [7]. Différents facteurs peuvent être également à l'origine de ces légères fluctuations (nourriture, salinité, température et physiologie) [8].

Enfin, les concentrations en métaux lourds Chez la palourde du lac Mellah sont faibles et les valeurs enregistrées sont inférieures aux concentrations limites autorisées dans différents pays pour la consommation de produits marins [9].

L'analyse des métaux lourds dans les palourdes recueillies dans le lac Mellah a montré que la contamination de cette espèce se trouve à un niveau faible. Il ressort de cette étude que les palourdes du lac ne semblent pas être polluées par les métaux lourds. Toutefois, il conviendrait de continuer la surveillance dans ce lac et d'étendre ce travail à d'autres espèces vivant dans le lac et de faire les dosages dans d'autres compartiments.

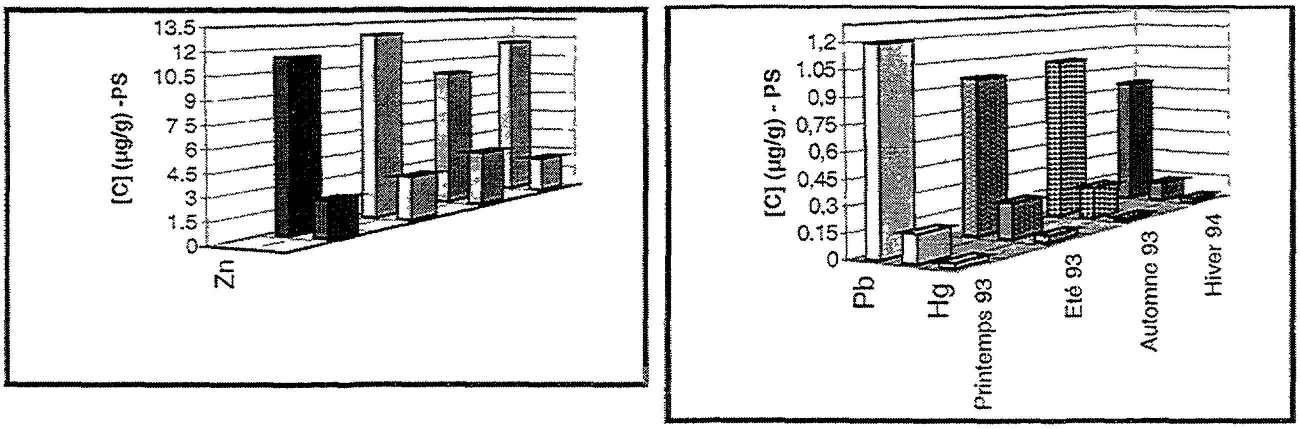

FIG. 2: Variations saisonnières des concentrations moyennes des métaux étudiés chez Ruditapes decussatus du Lac Mellah.

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IAEA-SM-354/130P

DETERMINATION OF RADIONUCLIDES PRODUCED BY ANGRA I NUCLEAR POWER PLANT IN MARINE SAMPLES COLLECTED IN THE BAY "SACO DE PIRAQUARA DE FORA" - ANGRA DOS REIS CITY - RIO DE JANEIRO

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Since 1985, Angra I Nuclear Power Plant, in Itaorna Bay, Angra dos Reis City, is in commercial operation, and produces 645 MW.

The plant, sometimes, releases liquid efluents to the environment. The activities of the possible radionuclides present in water, are checked, and they are only authorized if these activities are under the maximum permissible concentrations established by Comissão Nacional de Energia Nuclear (CNEN), the nuclear control institute in Brazil.

The Environmental Monitoring Laboratory was created in 1978 to monitore all the environment around Angra I NPP. This started since pre-operational time and goes on today, during normal operation.

The purpose of the work is to decribe the activities of the Laboratory in the collection and analysis of the marine samples: beach sand, sea water, fish, algae and sediments - which can be reached by an inadverted release, and to supply the results of the activities produced by the artificial radionuclides released by the reactor - Cesium-134 and Cesium-137, Cobalt-58 and 60, Iodine-131, Manganese-54 and Tritium - that can be found today and then compare them with the pre-operational period [1]. The Figure 1 shows the location of the collection points of the samples.

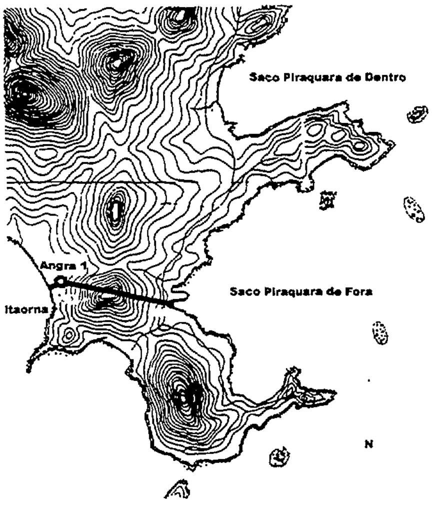


FIG. 1: Location of the Collection Points

The methodology used in the collection, preparation and analysis follows the international standards.

The marine sediments and beach sand are sifted using 16 mesh sieve to remove undesired material. The ashes are dried in an oven (110°C) and placed in an appropriated flask to count during 60,000 seconds.

The algae samples are washed with sea water and destilled water and calcinated in a furnace with progressive heating to 400°C. The ashes are analysed to determine the radioactive elements during 60,000 seconds.

The resident and moving fish have the meat removed, placed in trays and calcinated in a furnace (400°C). The ashes are placed in appropriated flask and analysed during 60,000 seconds.

The collected sea water, is taken to the laboratory and filtered to eliminate dust. The filtered water is placed in a 4 L marinelli beaker and analysed during 10,000 seconds to determine the radioactive elements. Tritium is analysed by liquid scintillation counting.

The results obtained by the Environmental Monitoring Laboratory, from the pre-operational period till now, are shown in Figure 2 (marine sediments), Figure 3 (algae), Figure 4 (moving fish) and Figure 5(resident fish).

The results obtained for all marine sediments, algae and fish samples (moving and resident), give us the indication that there are no changes in the artificial radionuclide activities. The actual values are the same than those of the pre-operational period and are below the limits specificated in Regulatory Guide 4.8[2]. The results obtained for all beach sands and sea water samples are below the Minimum Detectable Activities of the Laboratory. This shows that in spite the plant is operating conveniently since 1982, we still worry for the preservation the environment.

Figure 2 MARINE SEDIMENT

PRE-OPERATIONAL (1978-1982) - 1997

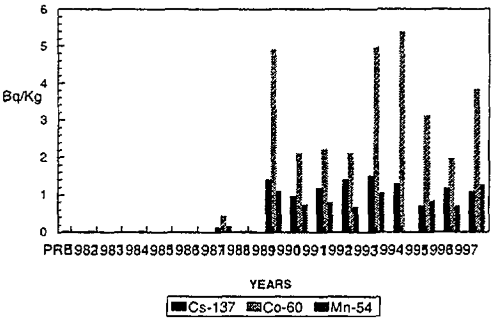
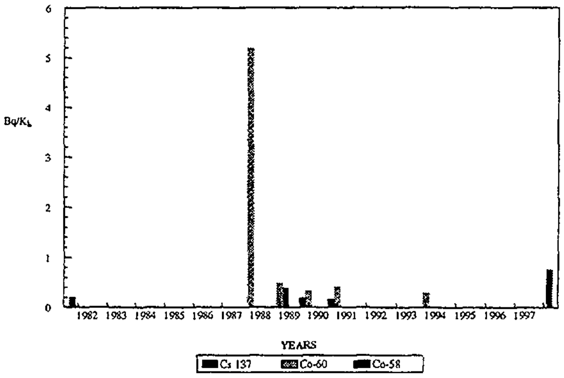


Figure 1 ALGAE

PRE-OPERATIONAL (1978 1982) - 1997



*PRE-1989 UNITS IN pCi/g

Figure 5 MOVING FISH

PRE-OPERATIONAL (1978-1982) - 1997

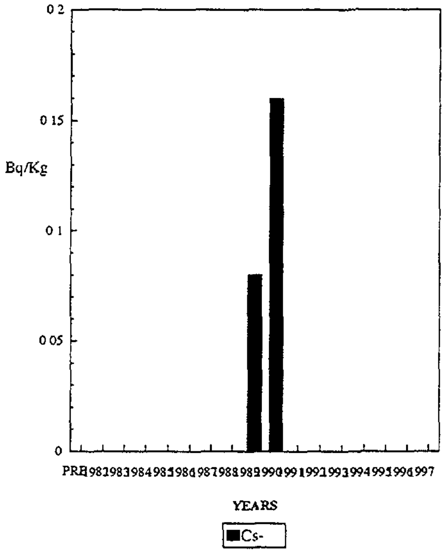
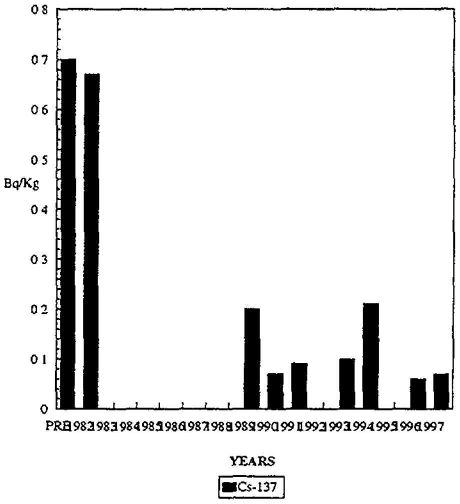


Figure 5 RESIDENT FISH

PRE-OPERATIONAL (1978-1982) - 1997



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THE FLOW OF RADIONUCLIDES THROUGH THE CANADIAN ARCHIPELAGO

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The transport of contaminants to the Canadian Arctic by air and in water and their concentration through the marine food web has lead to enhanced levels of contaminants in several foods of Canadian northern inhabitants. Artificial radionuclides in the marine water can be used to determine water circulation and to trace contaminant transport through the Canadian Archipelago.

The flow of water through the 16 passages of Canadian Archipelago from the Canada Basin of the Arctic Ocean to the west to Baffin Bay to the east is significant, contributing an estimated 2 Sv, or 25 percent of the inflow for Baffin Bay [1]. Flow is restricted to the surface water especially in the central region by the shallow sills present in each passage (Table 1) which range from 120 m to 250 m. The Arctic Ocean surface water is modified as it flows through the Archipelago. The halocline is warmer than in the Arctic Ocean due to diffusive flux of heat from the underlying warm Atlantic layer and there is freshwater input from rivers and ice melt

Recent radionuclide measurements in the Arctic Ocean indicate that levels of ^{129}I and ^{137}Cs have been increasing in Atlantic water of the Arctic Ocean. ^{129}I, whose main source is the nuclear reprocessing plants in Britain and France, clearly marks recent Atlantic source water. Atlantic water also provides most of the sources for ^{137}Cs which include nuclear fallout from weapons tests, the Chernobyl accident as well as the European reprocessing plants. The levels of ^{129}I and ^{137}Cs are used to determine the contribution of Atlantic water to water flowing through the Canadian Archipelago in various passages. Ratios of ^{129}I to ^{137}Cs, corrected for ^{137}Cs inputs from the Pacific Ocean, have been used to estimate transit times from the Norwegian Coastal Current to various locations in the Arctic Ocean [2].

TABLE I. MINIMUM SILL DEPTH FOR MAJOR PASSAGES IN THE CANADIAN ARCHIPELAGO

Passage	Sill Depth (m)
Hudson Strait	125
Lancaster Sound	125
Jones Sound	120
Nares Strait	250
Davis Strait	675

A time series of measurements of artificial radionuclides, including measurements from the 1970s, 1980s and 1990s, in Baffin Bay, the Beaufort Sea and the Canadian Archipelago is used to trace the flow in and out of the Canadian Archipelago. Profiles of these radionuclides in Baffin Bay over time reflect the decay of fallout radionuclides, the input from Chernobyl and European reprocessing plants via the West Greenland Current and the Arctic Ocean.

The ^{137}Cs distributions across Davis Strait reveal elevated levels flowing north in the West Greenland Current. ^{137}Cs levels have decreased since 1982 when surface levels of 4 to 5 mBq/l in western Baffin Bay were measured. ^{129}I distributions in 1997 indicate some input from European reprocessing *plants (> 5 x 10^7 at/l) in surface water. Although the distribution of ^{137}Cs is similar, activities across* Hudson Strait have been halved from 1983 to 1997.

Samples collected for radionuclide analysis in the Canadian Archipelago in 1997 provide some of the first data from this area. Cross sections of ^{137}Cs and ^{129}I distributions from Beaufort Sea to Baffin Bay via Lancaster Sound along latitude 74°N reveal slightly elevated activities in bottom water indicating the transport of arctic-source Atlantic water through Barrow Strait.

Water flows north into Baffin Bay from the Labrador Current and the West Greenland Current. The northerly flow of the West Greenland Current (low salinity and enhanced ^{137}Cs levels) in Baffin Bay was traced in surface water samples in 1984 and 1986. Enhanced levels of ^{137}Cs were observed in 1986 are a result of added Chernobyl inputs. Low ^{137}Cs levels correspond to high salinity samples when samples were collected outside of the West Greenland Current.

^{137}Cs and ^{129}I levels are higher in Nares Strait, with its deeper connection to the Arctic Ocean, compared to Jones Sound, particularly at depth. ^{129}I levels in Nares Strait and Jones Sound deep sample (> 5 x 10^7 at/l) show input from the European reprocessing plants via the Arctic Ocean.

- Radiotracers provide new insight into water circulation in the Arctic Ocean, Baffin Bay and the Canadian Archipelago.
- Significant decreases in ^{137}Cs activities have occurred in Baffin Bay between 1980 and 1997 as a result of decay of fallout radioactivity.
- The transport of Atlantic water from the Arctic Ocean through Nares Strait into Baffin Bay is evident from the above-fallout levels of ^{129}I (> 5 x 10^7 at/l).
- The radionuclide levels in the Atlantic water in the Arctic Ocean are increasing due to the arrival of enhanced releases from European reprocessing plants.

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XA9952019

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RADIOLOGICAL STUDY OF BARDAWILL LAKE IN EGYPT

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Bardawill Lake is one of the five northern lakes which are originally bodies of the Mediterranean sea water and located at the very north of Egypt. Bardawill Lake is located in the northern part of Sinai peninsula between 31^0 02 and 31^0 14 N; and 32^0 40 and 33^0 37 E. It covers an area of about 600 km^2. It is about 80 km long and its maximal width is about 18 km. The water depth ranges from few centimeters to about 2.9 m. It is connected with the sea through three inlets, two of which are kept artificially open by periodical dredging, while the third is natural. The lake water is actually a mixing of local groundwater with the sea water. The salinity ranges from 46.6 to 81.1 g/l. The annual fish production is about 2500 tons (65% Bream, 20% Mullets, 6% seabass, 5% Sole and 3% others). Fishing is banned yearly for four months in order to allow fish to reproduce and to grow reaching marketable size [1,2].

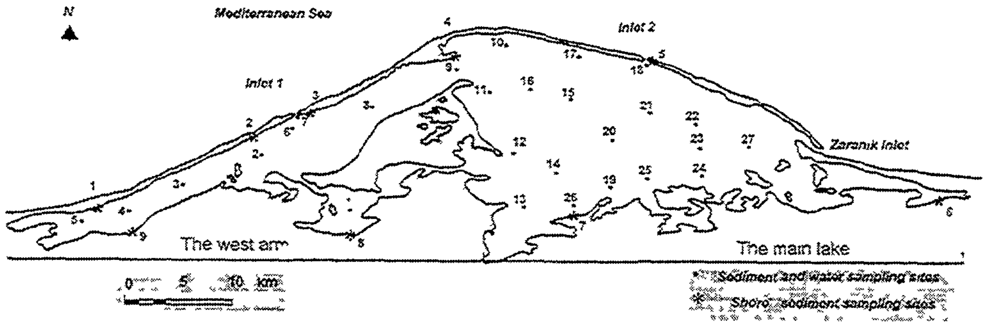

FIG.1. Sampling sites for bottom and shore sediments and water samples in Bardawill Lake.

Twenty six bottom sediment (BS) samples, twenty six water samples, nine shore sediment (SS) samples (Fig 1) and 36 fish samples of all above mentioned types of fish were collected.
For Gamma-spectroscopy Analysis (GA) the bottom and shore sediment samples were dried at 115^0 C, crushed, sieved through 1 mm mesh size, homogenized and transferred to Marinelli beakers. The beakers with samples were sealed for 4 weeks to reach secular equilibrium between Radium-226 (of the U-238 series) and daughters. The water samples were acidified (with nitric acid to avoid micro- organisms' growth and to minimize water-walls interaction), stored in polyethylene containers for transportation to the laboratory.

The fish samples obtained from the professional fishers were washed thoroughly and filleted. The head with the bone (HB) and the flesh (F) were dried separately at 80^0 C. Every dried sample was milled and transferred to air tide polyethylene container of 100 or 250 ml capacity.
For Alpha - spectroscopy Analysis (AA) selected 6 bottom sediment samples with 60-100 mBq U-232 tracer is dissolved. For uranium separation, the dissolved sample goes through steps of chemical extraction, co-precipitation, ion-exchange and electro-deposition on stainless steel disk [3].

Using γ-spectrometers based on HPGe-detector in a lead shield with two internal cadmium and copper cylinders, the bottom sediment and shore sediment samples, water samples, fish flesh samples and head & bone samples were analyzed after absolute efficiency calibration of the spectrometer [4] . The average specific activity of Ra-226 (of the U-238 series) , Th-232 series, K-

40 and Cs-137 in Bq/kg (dry weight)for 26 bottom sediment (BS)and 9 shore sediment (SS) samples is given in Table I. In brackets the range of specific activity variation is given.

For the analyzed water samples, the K-40 radionuclide was the only one with concentration higher than the detection limit of the spectrometer. The average K - 40 concentration of the analyzed 26 samples is 18.3 Bq/l and the values of individual concentration ranged between 11.7 and 30.5 Bq/l. The same concentration was measured using flame fluorimeter and was found to have average value of 19.9 Bq/l (14.9-26.6 Bq/l). The average values (and the range of variation) of the concentration of Ra-226 (U-238), Th-232, K-40 and Cs-137, in Bq/kg (dry weight) in the analyzed 36 fish flesh (F); and 30 fish head and bone (HB) samples are given in Table II.

TABLE IRADIONUCLIDES IN SEDIMENTS

Samples	Ra-226	Th-232	K-40	Cs-137
BS	6.79	4.46	185.6	2.51
[26]	(3.3-13.6)	(2.32-9.11)	(94.9-258.8)	(0.10-6.50)
SS	3.82	2.40	108.4	0.19
[9]	(2.49-7.45)	(1.65-4.81)	(67.8-197.6)	(0.10-0.55)

TABLE II RADIONUCLIDES IN FISH SAMPLES

Samples	Ra-226	Th-232	K-40	Cs-137
F	3.03	1.43	320.7	0.42
[36]	(0.6-5.58)	(0.5-2.69)	(129.7-470.9)	(0.1-1.43)
HB	3.90	2.07	219.3	0.43
[30]	(0.6-7.65)	(0.6-4.73)	(94.6-450.1)	(0.1-1.37)

Using an Alpha spectrometer based on surface- barrier detector, six bottom sediment (BS) samples collected from different sectors of the lake were analyzed. The specific activity of U-238,U-235, total uranium (Bq/kg dry weight) and the ratio of U-234/U-238 are given in Table III.

TABLE III RADIONUCLIDES IN SEDIMENT SAMPLES

Sample Code	U-238	U-235	Total U (cal.)	U-234/238
BS4	61.6±3.1	4.90±0.59	128.8±6.9	1.01±0.07
BS9	9.8±1.1	0.34±0.20	17.9±2.2	0.79±0.13
BS14	49.8±6.3	1.12±0.66	114.2±14.5	1.27±0.22
BS18	49.5±6.3	1.72±0.45	104.0±7.3	1.07±0.10
BS21	45.7±2.7	0.62±0.21	90.9±5.5	0.97±0.08
BS27	55.9±5.9	2.36±0.81	107.6±12.1	0.88±0.13
Ave.	45.4	1.84	93.6	0.99

The absorbed dose equivalent in µSv / due to the ingestion of Ra-226 (of the U-238),Th-232 and K-40 resulting from flesh consumption of 7 Kg/y of fish was calculated [5] for the 36 collected fish samples. The average equivalent absorbed dose is found to be 25.8 µSv/y with range of variation from 9.9 to 43.1 µSv/y. The contribution from Ra-226, Th-232 and K-40 to the average dose is 7.5, 7.1 and 11.2 µSv/y respectively.

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Pu-239+240 AND Pu-238 DISTRIBUTION AMONG DISSOLVED, COLLOIDAL AND PARTICULATE PHASES IN THE RHONE RIVER (FRANCE)

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The Rhône River is the major source of terrigenous and freshwater inputs to the Norhwestern Mediterranean Sea. Plutonium nuclides reach the Rhône River system through the weathering and erosion of surface soils contaminated by the global fallout from atmospheric nuclear tests, and the liquid effluent discharges from the Marcoule nuclear fuel reprocessing plant (Fig.1). To substantiate geochemical behavior of transuranium nuclides and to estimate their availability and toxicity towards organisms needs the study of their chemical and physical forms in natural water systems.

The determination of plutonium distribution among dissolved, colloidal and particulate phases was investigated in the Rhône River at Arles, 50 km upstream the river mouth, in May 1997. The flow rate of the river reached its average annual value (i.e., 1800 $m^3\ s^{-1}$). 1100 l of fresh water were collected, a part (900 l) was prefiltered on 1200 and 450 nm, then ultrafiltered by sequential ultrafiltration. For operational details see[1].

Non filtered (total), filtered (<450 nm) and ultrafiltered (<2 nm) samples were analysed for plutonium content after co-precipitation with $Fe(OH)_3$ and using radiochemical procedures by solvent extraction and/or cation exchange. Upon radiochemical separation, plutonium alpha sources were preparated by electrolytic plating onto stainless-steel discs.

Contrarily to Pu nuclide activities in the Rhône sediments, very few data are available concerning the Rhône River freshwater. Pu-239+240 and Pu-238 activities measured in the non filtered sample reached 43,8 ± 2.3 μBql^{-1} and 17,8 ± 1.3 μBql^{-1} respectively (Table I). These activities are lower (-35%) than in August 1989 [2].This can be related both to a higher Rhône River flow (i.e., radionuclides dilution) and the decrease in Pu discharges since 1991 (1/400) due to new treatment processes of the Marcoule liquid effluent [3]. The Pu-238 /Pu-239+240 activity ratios (AR) measured in the various fractions are not significantly different reflecting as expected the same physico-chemical behavior of the various Pu isotopes within particulate, colloidal and true dissolved phases. The average AR value is 0.40 ⌖ 0.08 which is characteristic of the Marcoule plant's liquid effluent [4]. Our results indicate than in the Rhône River under moderated flow rate, 85% and 9% of the total plutonium is associated with particles > 450 nm and colloidal substances (2-450 nm) respectively. Indeed, Thomas [5] observes that in the Rhône river, the transport of plutonium is largely under the particulate form. Although some observations have been recently made on colloidal plutonium association in sea waters [6] and in the Shellafield plant effluents [7], data on plutonium association with colloidal compounds in natural freshwaters are very scattered. Nevertheless, the observations reported by [8] and [9] showing an important plutonium affinity for colloidal substances in groudwaters and superficial freshwaters are consistent with our results.

TABLE I. Pu-239+240 AND Pu-238 ACTIVITIES ($\mu Bq\ l^{-1}$) AND Pu-238 /Pu-239+240 ACTIVITY RATIOS (AR) IN THE RHONE RIVER (1800 $m^3\ s^{-1}$, AVERAGE ANNUAL FLOW RATE: 1700 $m^3\ s^{-1}$).

	Pu-239+240	Pu-238	AR
Total	43,8 ± 2.3	17,8 ± 1.3	0,41 ± 0.04
<450nm	6,67 ± 0.66	2,72 ± 0.42	0,41 ± 0.07
<2 nm	2,74 ± 0.47	1,04 ± 0.32	0,38 ± 0.13

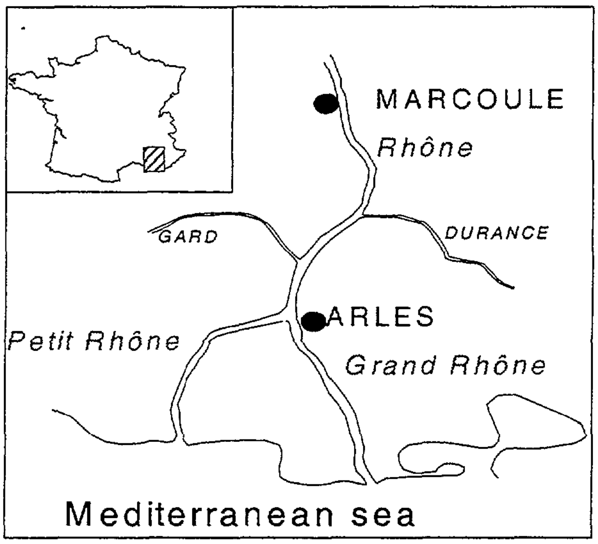

FIG. 1. Sampling area.

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MARINE POLLUTION IN CAMEROON (GULF OF GUINEA): STATE AND REMEDIES FOR SUCCESSFUL CONTROL AND MONITORING

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Cameroon is situated at the base of the Gulf of Guinea, and opens into the Atlantic Ocean with a coastline of about 402 km. The Gulf of Guinea is a semi-closed milieu, with two opposing groups of currents: the Benguela and the sub Equatorial currents from the southern sector, on the one hand, and the Guinean current, the Equatorial counter current, and the Canary current from the north, on the other hand (Table I). Pollution control in this region, with its complex and poorly understood circulation, is of prime importance to the coastal community and should be considered in global terms, so as to arrive at integrated solutions within a regional context. In effect, the countries of the Gulf of Guinea sub-region share almost the same oceanographic conditions and marine resources. They all experience the same problems in connection with marine pollution control and the integrated management of their coastal zones.

This paper analyses the various research results obtained over several years in Cameroon on coastal and marine pollution, especially pollution by solid wastes, industrial and domestic effluents, hydrocarbons (tar balls), heavy metals and pesticides. Values in the order of 175,531 and 194,685 tons have been estimated for annual pollution loads in terms of BOD and suspended matter respectively [1]. With respect to BOD, the most polluting industries are petroleum refineries, food processing and chemical industries which respectively represent 38, 36 and 10% of the total annual BOD. Measurement of tar balls on various Cameroonian beaches (Table II) shows values as high as 42.40 g/m^2 of beach, while the concentration of heavy metals (Table III) encountered in shrimps and fish consumed in Cameroon shows a very wide range of values. Most of these values are similar to those obtained within the region, and some are alarming in their magnitude.

The countries of the region have become aware of the problems of marine pollution. Thus, the government of Cameroon has adopted its National Environmental Management Plan (NEMP), in which marine pollution is given high priority; the NEMP calls for the integrated management of marine and coastal zones. High risk zones have been identified. Control and monitoring programmes have been set out, but their execution is hampered by financial difficulties, absence of target-oriented research and conflict of competence between various ministries involved in the management of the coastal zone; existing legislation in the domain is inadequate and ill-adapted. The absence of national norms on marine pollution makes the situation even more difficult. Results so far obtained are insufficient, with regards to the problems encountered.

TABLE I. SPEEDS (m/s) AND TYPE OF CURRENT IDENTIFIED IN THE GULF OF GUINEA [2]

Current type	Dec-Jan-Feb.	Mar-April-May	June-July-Aug.	Sept-Oct-Nov
Canary current	0.15	0.15	0.15	0.15
Equatorial counter current	0.30	0.21	0.24	0.18
Guinean current	0.24	1.30	0.51	0.30
Sub-equatorial current	0.21	0.24	0.45	0.24
Benguela current	0.24	0.15	0.15	0.15

To reduce marine pollution in Cameroon and in the Gulf of Guinea in general, and ensure better control and monitoring, it would be necessary to: compile an inventory of existing texts relating to marine pollution and adapt them to the current situation, create a committee to set norms for various types of pollution in each country, adopt a standard methodology at the regional level for studying and measuring marine pollution. Education and sensitisation of the population should be a priority, and should be carried out through the public media and NGOs. Users of the coastal and marine zone should be involved in the planning and development of all activities related to marine pollution.

TABLE II. TARBALL CONCENTRATION ON VARIOUS BEACHES OF THE CAMEROON COAST (g/m^2), [3,4,5]

Locality	Type of beach	Length or surface area sampled	weight g/m^2 or g/m
Limbe Dockyard [5]	fine sand	50 m^2	01.55
Limbe Mile Six Beach [5]	fine sand	600 m^2	02.98
Essongo (Debundscha) [3]	fine sand	400 m^2	04.40
Souelaba Point (Wouri Estuary) [4]	fine sand	100 m^2	00.00
Sanaga Estuary [4]	fine sand	10 m^2	32.05
Lokoundje Estuary [4]	fine sand	400 m^2	16.34
Londji (near Kribi) [3]	fine sand	100 m^2	00.00
Limbe Bota [3]	rocky	75 m	42.40
Debundscha [1]	coarse sand	175 m	03.70

TABLE III. MEAN METAL CONCENTRATIONS IN MARINE FISH (mg/g FRESH WEIGHT) IN THE GULF OF GUINEA COUNTRIES.

Location	Hg	Cd	Pb	Cu	Zn	Reference
Fin fish						
Côte d'Ivoire	0.11	< 0.25	---	< 0.80	4.55	[3]
Ghana	0.064	< 0.10	0.36	0.46	4.63	[4]
Ghana	0.24	---	---	---	---	[5]
Nigeria	---	0.10	2.28	11.3	27.5	[6]
Cameroon	0.09	0.26	---	---	---	[7]
Cameroon	0.06	< 0.10	1.83	0.75	5.55	
Shell fish, Penaeus						
Côte d'Ivoire	0.042	< 0.25	---	6.02	17.9	[3]
Ghana	0.033	< 0.10	0.82	6.16	14.9	[5]
Nigeria	---	0.18	5.10	23.6	2.40	[7]
Cameroon	0.057	< 0.10	---	---	---	
Cameroon	0.070	0.21	---	9.5	40.4	
Crassostrea sp						
Côte d'Ivoire	0.125	0.65	---	24.5	1205	[8]
Nigeria	---	0.17	2.09	5.80	628	[5]
Cameroon	0.072	0.56	---	---	407	[6]
Cameroon	0.083	0.25	---	8.45	213	[7]
Cameroon						
Pseudotolithus typus	---	---	---	2.20	0.25	[9]
P. Elongatus	---	---	---	0.39	0.23	[9]
P. Senegalensis	---	---	---	0.47	0.28	[9]
Ethmalosa fimbriata	---	---	---	0.42	0.26	[9]
WHO Limits	0.5	2.0	2.0	30.0	1000	[10]

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THE BARENTS SEA, DISTRIBUTION AND FATE OF RADIOACTIVE CONTAMINANTS

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The Barents Sea is the only part of the Arctic seas with a substantial biological production. The annual harvest of the fisheries has a potential outcome of between 2 and 3,5 million tons which represent about 3 - 5 % of the worlds fisheries. The special hydrographic regime with inflow of warm Atlantic water and formation of dense bottom water in the winter together with vertical mixing of nutrients and the intensive production at the ice-edge during the ice melting give the conditions for the high production of the Barents Sea.

Possible contamination in the marine food webs of the Barents Sea may be a problem for a rational harvest of the area. Radioactive contamination has in this context a special public impact as even traces of radioactivity seems to be considered by the public to be a real danger. It is therefor of special impor-tance, from a regulatory and fisheries point of view, to accumulate knowledge of the behaviour of radio-active elements in the marine ecosystems of the Barents Sea in order to place this contami-nation in proper and realistic pro-portions.

The most pronounced impact of radioactive contamination in the fish resources of the Barents Sea originated in the nuclear bomb tests that took place over the eastern part of the area in the late fifties and beginning of the sixties, culminating in 1963 as Fig. 1 demonstrates. As can be seen there are some differences in the degree of contamination in the various fish species, which may be explained by their difference in food preference. This indicate that transport through actual food webs can be of varying importance for assessing a potential contamination, thus a better knowledge of transfer mechanisms through various food webs is needed.

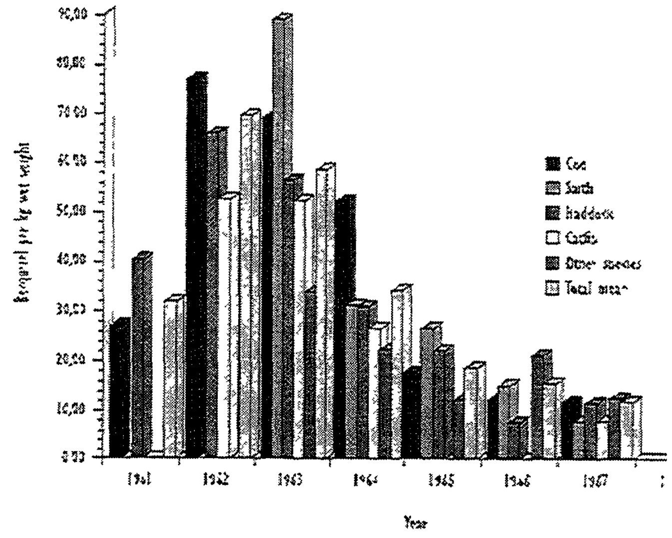

FIG. 1. Total mean beta-activity minus potassium-40 measured in various fish species from the Barents Sea [1].The 1991 - 98 values are for cesium-137 and reported by [2] for the years 1991-94 and for 1995-98 by the Norwegian Radiation Protection Agency (NRPA).

The monitoring, by IMR, of radioactivity in fish from the Barents Sea ended in 1968 and was based on a method for determining total-beta minus potassium-40. Then following the Chernobyl accident and the information of dumping of radioactive material by the former Soviet Union again arouse public concern about possible radioactive contamination of the fish resources and new sampling was established. The present degree of contamination in fish from the Barents Sea is, however, almost negligible as can be seen from Fig.. 1. Contamination in bottom-sediments reflects the more long-term impact and may also indicate the original source and transport routes for the various contaminants. Fig.. 2 presents our data of the Cs-137 content in the upper 2 cm of the bottom-sediments. The maximum sedimentation rate in the Barents Sea is measured to about 0,2 mm per year and consequently the upper 2 cm should cover the sedimentation of100 years under the assumption that bioturbation has not changed the vertical distribution in the sediments [3]. We may therefor assume that our data will cover the total anthropogenic load to the bottom-sediments of the Barents Sea.

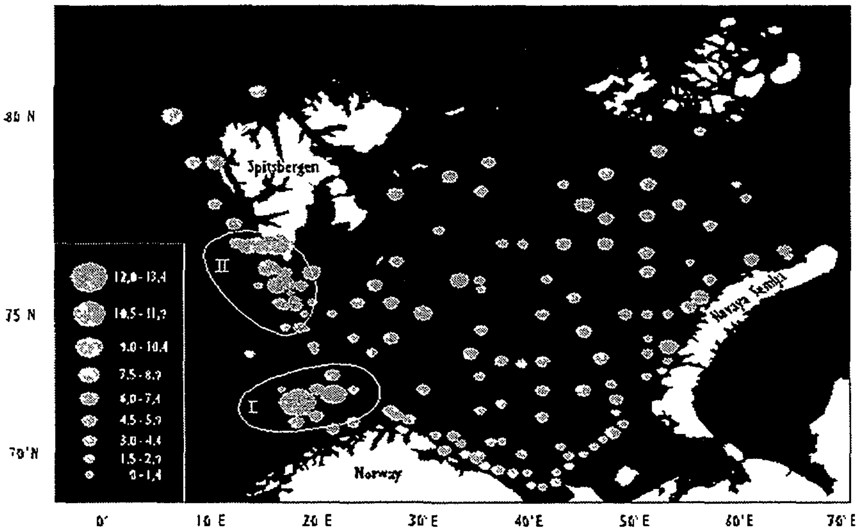

FIG.. 2. Cesium-137 values in bottom sediments of the Barents Sea from the years 1991 to 1998, values in Bq/kg dry weight.

The distribution indicate particularly two areas (Fig.. 2), I and II, with a higher load of Cs-137, both areas are located in the western part of the Barents Sea. Area I is found in a highly productive bank-area where the residence time for the water is prolonged due to the bottom topography. Area II between Bear Island and Spitsbergen represents a more or less permanent polar-front area. From Fig.. 3, where temperature profiles between Bear Island and Spitsbergen are presented, the vertical mixing-zone between the cold and the warm water is clearly seen. Both areas are characterised by high primary production and we may therefor assume that this production acts as a trap for contaminants in the water masses passing through the areas [4].

While the transport of Cs-137 to the bottom in area I, where the water-masses is stratified, is most likely to be a passive transport via dead phytoplankton, the sedimentation in area II may well be an active transport via living phytoplankton. An active uptake of radionuclides in phytoplankton may then govern the direction of the transport of contaminants through the various food webs. And as indicated in Fig.. 1 there were differences in the degree of contamination of fish species feeding mostly in different food webs.

Four sources for the radiocesium contamination of the Barents Sea sediments can be distinguished. The major impact seems to be the transport from the European nuclear industry and Chernobyl run-off particularly to the Baltic, via the Norwegian coastal current entering the Barents sea from south-west (Fig.. 2, area I). This transport is also reflected in area II where the West-Spitsbergen branch of the coastal current passes by.

Fall-out from the earlier atmospheric bomb test and the Chernobyl accident is likely the source for the increasing contamination we measured inwards the southernmost fjord in Spitsbergen. Transport by ice from east of Novaya Semlja and the Siberian shelf [5, 6] may be the source for the slightly elevated levels found in the wide melting zone for ice in the North-eastern part of the Barents Sea.

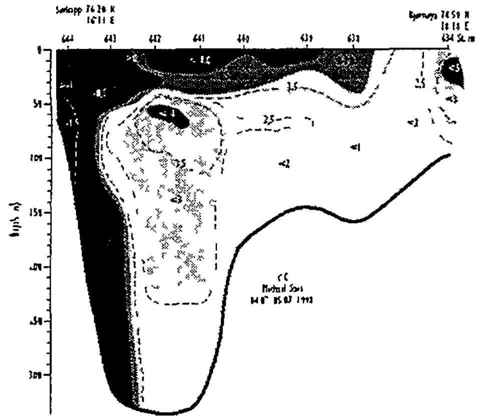

FIG 3. The vertical temperature distribution in a cross section from the Bear Island to Sørkapp on Spitsbergen in the beginning of July 1998.

The present radioactive contamination of the Barents Sea is almost negligible. But there is a precautionary need to study the various transport routes through the food webs to be able to assess a possible impact on the fish resources should an accident with release of radioactive material take place in the future. To study various transport routes through the food webs is a tideous work. Due to the special production patterns in polar front areas, we want to focus on the role phytoplankton may have in the transport of radionuclides from the water phase to higher trophic levels. This will be done by both field-studies and controlled laboratory experiments.

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PRODUCED WATER FROM OFF-SHORE OIL AND GAS PRODUCTION, A NEW CHALLENGE IN MARINE POLLUTION MONITORING

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Produced water consists of water naturally present in the oil and gas reservoir (formation water), flood water previously injected into the formation, and/or, in the case of some gas production, condensed water. Produced water is part of the well stream together with oil and/or gas.

Oil and/or gas are separated from the produced water on the production platform. The produced water is treated to reduce the dispersed oil content to below the regulatory maximum limit of 40 mg/l, set by OSPAR, before it is discharged from the production platform. Most oil companies claim that they normally reduce the oil content to below 20 mg/l.

Produced water is the largest volume waste stream in the exploration and production process of oil and gas. Over the economic life of a producing field, the volume produced water can exceed by ten times the volume of hydrocarbon produced. During the later stages of production, produced water can account for as much as 98 % of the extracted fluids.

Typical water production rates from oil platforms are from 2 400 to 40 000 m^3/day and for gas platforms 1,6 - 30 m^3/day [1]. This amounts to an expected discharge of produced water to the North Sea in 1998 of $3,4 \times 10^8$ m^3.

When discharged the produced water still contains a wide range of components:
dissolved organic components, various production chemica trace metals, naturally occurring radioactive material, inorganic salts.

In addition the discharged water is almost depleted for oxygen and has an average COD or BOD value of 4 000 mg O_2/l [1].

Of the dissolved organic components carboxylic acids account for the major organic load with concentrations in the discharged produced water ranging from 30 - 930 mg/l. Other major components dissolved in the produced water are BTEX-components (Benzene, Toluene, Ethyl Benzene and Xylenes) in concen-trations from 0,5 - 14 mg/l for oil platforms and from 5 - 630 mg/l for gas platforms, phenols in concentrations between 1 - 23 mg/l and polycyclic aromatic hydrocarbons (PAHs) in concentrations ranging from 40 - 1 600 Fg/l, with naphthalene (40 - 1 600 Fg/l), phenanthrene (10 - 500 Fg/l) and dibenzo-thiophene (10 - 170 Fg/l) representing the majority [1,2,3].

In addition to the organic components trace elements as Pb, Cd, Cu, Hg, Ni, Zn, As and Cr are dissolved in the produced water in considerably greater concen-trations than in sea water.

The Naturally Occurring Radioactive Materials (NORM) in discharged water consists mainly of ^{226}Ra and ^{228}Ra representing more than 90 % of the total radioactivity in the produced water. The radium concentration in produced water can be from 100 - 1 000 times the naturally concentration of sea water.

Bicarbonate (615 mg/l), chloride (44 g/l) and sulfate (814 mg/l) are the main inorganic salts discharged.

The production chemicals consist of a wide range of products, but they are all supposed to be treated according to national and international (OSPAR) regulations.

The discharge of produced water is a continuous process and based on an expected amount of 340 million m^3 discharged in 1998 the total amount of some environmental important components can be calculated in Table I.

The figures in the Table are calculated from an assumed average concentration. But both composition and concentration change from well to well and throughout the lifetime of the production wells. As the discharge of produced water is a continuous process there will be established a certain area around the platforms where there is a more or less permanent influence of produced water. In areas with a high density of oil and gas fields the influence area of one platform overlaps the influence area of nearby platforms. Fig. 1 shows an example of a modelled influence area of produced water

TABLE I AN ESTIMATION OF THE AMOUNT OF SOME DISSOLVED COMPONENTS AND DISPERSED OIL IN PRODUCED WATER, DISCHARGED INTO THE NORTH SEA FROM OIL AND GAS EXPLOITATION IN 1998 THE CALCULATIONS ARE BASED ON AN ESTIMATED DISHARGE OF 340 MILLION CUBIC METERS PRODUCED WATER INTO THE NORTH SEA IN 1998

Average concentration	Carboxylic acides 500 mg/l	BTEX 8 mg/l	Phenols 5 mg/l	PAHs 500 Fg/l	Hg 5 Fg/l	Cd 10 Fg/l	Dispersed oil 20 mg/l
Total input	170 000 t	2 700 t	1 720 t	172 t	1,72 t	3,4 t	6 800 t

from discharges from oil-fields in the Tampen area in the northern North Sea The crosses represents oil- and gas-fields that also are discharging produced water, but which are not included in the modelled distribution.

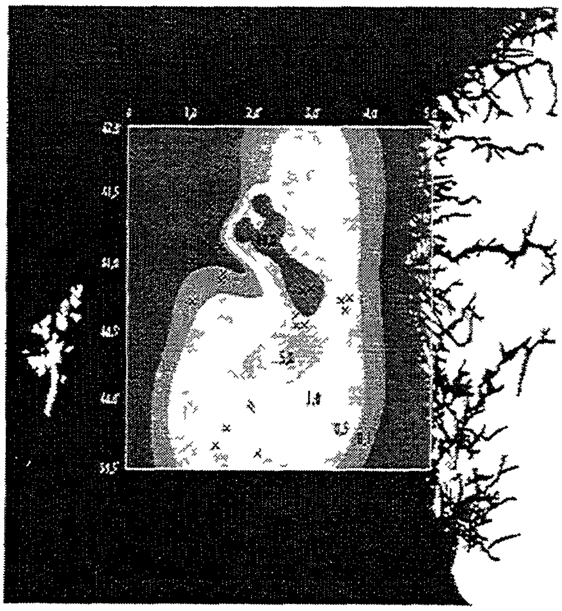

FIG 1 Modelled horizontal distribution of concentration fields in percent of produced water in 0 - 25 m, in a summer situation of discharges from oil platforms within the Tampen area, in the northern North Sea [2] X indicates nearby oil and gas platforms which also discharge produced water, but which are not included in the modelled distribution

Most of the discharge points for the produced water are located at some depths beneath the sea surface. Fig 2 shows the modelled vertical distribution of the produced water from the oil-fields in the Tampen area in a summer and winter situation. As can be seen in Fig. 2, the plume of produced water occurs between depths of 25 and 50 meters and this is the part of the water column where most planktonic organisms are found.

Oil companies claim that the discharges from their activities only influence a very limited area around the platforms, and that at a distance of some few km from the discharge point the dilution has reduced the contamination to a non detectable level. They also claim that evaporation and biological degradation are important factors for reducing the degree of contamination. Evaporation may certainly be an important factor for the lighter component like the BTEX and phenols provided that they are found in the surface, but if the modelled vertical distributions demonstrated in Fig. 2 represent the normal behavior of the produced water, evaporation can hardly be of specially grate importance.

Carboxylic acids may act as a growth medium for bacteria and therefor such bacterial growth may change the abundance and the composition of the marine bacteria communities and thereby change the basis for organisms at a higher level in the food chains, feeding on bacteria. The problem of monitoring and assessing the impact of produced water have recently been raised within the Working Group of Environmental Assessment and Monitoring Strategies (WGEAMS) of the International Council for the Exploration of the Sea (ICES). WGEAMS pointed to a range of studies

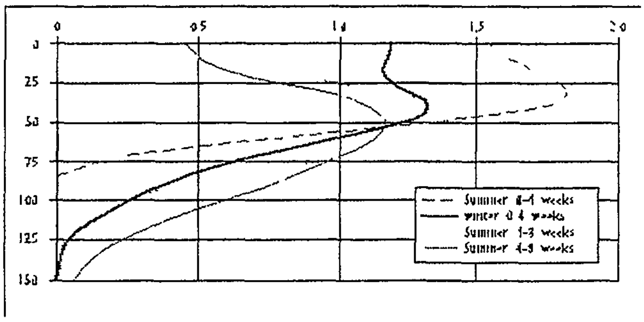

FIG 2. Modelled vertical distribution (depth in meters) of produced water, discharged in 8 week periods during summer and winter months. The distributions are given as percent share per depth meter [2]

and activities needed to be undertaken should the possible problems created by the increasing discharge of produced water be properly assessed. WGEAMS mentioned among others the need for development of new tests for chronic effects on fish eggs/larvae, the need for regional studies to investigate effects on pelagic communities from bacteria through phytoplankton to zooplankton and modelling results should be verified by field surveys [4].

As the oil exploration moves northwards to colder waters along the Norwegian coast and in to the Barents Sea, into areas where most of the important fish resources of the Northeast Atlantic have their spawning and breeding areas we fear that the chronic exposure from produced water can affect the development of strong year classes of important fish stocks. It is therefor necessary to find practical methods for monitoring the fate of produced water both for the sake of reducing the existing suspicion of effects not yet detected or for documenting effects that can be used in the political decisions that have to be taken prior to further oil- and gas- field developments.

For the polluter, the oil companies, there is an urgent need to develop methods for continuous measurement of all dissolved components in the produced water. To day only the dispersed oil content are monitored regularly. For the purpose of assessing the impact of produced water the oil companies must be required to provide data on the composition and the amounts of discharged components.

So far, no acute toxic effects of produced water have been reported. The huge and increasing amount of produced water discharged to the sea, without any regulations from national or international regulatory bodies, seems however, to be an important threat to the marine environment and its living resources. The lack of knowledge is frightening, and the possibility that there is a sneaking ecosystem change that will not be detected before it may be to late is unfortunately evident. Both national and international authorities should give high priority to these problems at least in a precautionary context.

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ASSESSMENT OF THE ADRIATIC SEA-WATER MEAN RESIDENCE TIME USING FALLOUT ^{90}Sr AS RADIOACTIVE TRACER

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In physical oceanography ^{90}Sr can be used as radioactive tracer to study circulation of sea water. As a part of an extended monitoring programme, ^{90}Sr has been analysed in sea water samples and fallout on the Adriatic since 1963. Samples of surface sea water have been collected on four locations of the Adriatic Sea: towns of Rovinj and Rijeka in North Adriatic, town of Split in Mid-Adriatic and town of Dubrovnik in South Adriatic. Fallout samples have been collected monthly in the city of Zadar (Mid-Adriatic). ^{90}Sr activity concentrations are found to be approximately equal on all locations observed, not differing from the rest of the Mediterranean Sea [1]. It was estimated that approximately 85% of all man-made radioactive_contamination in the Mediterranean comes from fallout [2]. Consequently, in the Adriatic, ^{90}Sr activity concentrations are in good correlation with the fallout activity, the coefficient of correlation being 0.72 [1]. The elongated shape (some 800 by 200 km) and almost landlocked position of the Adriatic sea play an important role in dynamics of its water. The Adriatic sea is the major source of the densest water in the Eastern Mediterranean, the *Eastern Mediterranean Deep Water* (EMDW) [3]. Meteorological conditions favourable to dense water formation occurring during Bora events (the dominant winter wind blowing from Northeast), cause rapid mixing of surface waters with the intermediate water layer, which can therefore be considered as a single water reservoir (83% of the total Adriatic Sea volume). This is especially true for the North Adriatic since it is relatively shallow, the depth not exceeding 100 m. Together with the surface waters ^{90}Sr sinks to deeper water layers and eventually, due to the general circulation pattern, leaves the Adriatic. Assuming that most of the ^{90}Sr comes into the Adriatic sea by fallout, the ^{90}Sr circulation in the Adriatic sea can be described by the simple mathematical model:

$$\frac{d\,A_s(t)}{dt} = -(\,k_s + \lambda\,)\,A_s(t) + I(t)$$

where

$A_s(t)$	is the total, time-dependant ^{90}Sr activity (Bq) in reservoir consisting of surface and intermediate water, obtained by multiplying the observed activity concentration data by the volume of the reservoir (29,000 km^3),
λ	is the decay constant for ^{90}Sr (y^{-1}),
$1/k_s$	is the mean residence time of ^{90}Sr in a reservoir (y) and
$I(t)$	is the total annual ^{90}Sr input in to the Adriatic sea (Bqy^{-1}).

In order to solve the equation **(1)** several assumptions were made. It was assumed that the intermediate water entering the Adriatic from the Mediterranean (Ionian sea) does not significantly contribute to total ^{90}Sr inventory in the Adriatic due to a slower mixing rate of surface and intermediate waters. Also, it was assumed that the input of ^{90}Sr by the Po river is proportional to the direct fallout input. Therefore, the total input of ^{90}Sr to the Adriatic sea was estimated by multiplying the observed fallout data by the area of the Adriatic sea (138,600 km^2) and multiplied by factor 1.2 to adjust for the run-off contribution form the Po river. Finally, the fallout data obtained from the measurements in the city of Zadar were_assumed to be representative for the whole Adriatic area. The long-term fallout data were fitted to the equation:

where:

I_o is the initial input of ^{90}Sr in the Adriatic sea and

k_f is a constant.

By fitting the fallout experimental data for the 1963-1996 period (**Figure 1**), for k_f is obtained 0.39 y^{-1} and for I_o=I(1963) 135 TBq (812 Bqm^{-2}). After combining

$$I(t) = I_0 e^{-k_f t}$$

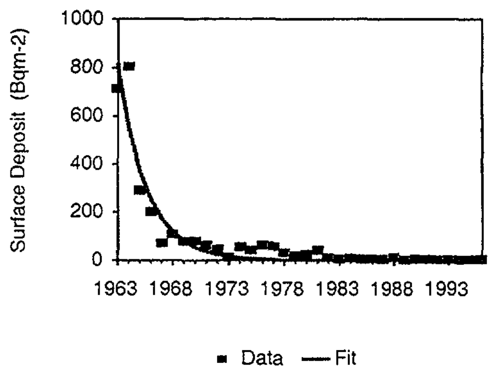

FIG. 1. Fitting the fallout data.

equations (1) and (2) and solving for A(t), with initial conditions I_o=I(1963) and $A_s(0)$=A_s(1963) the following solution is obtained:

$$A_s(t) = \frac{I_0}{k_s + \lambda - k_f} [e^{-k_f t} - e^{-(k_s + \lambda)t}] + A_s(0) e^{-(k_s + \lambda)t}$$

By fitting the experimental data to a theoretically predicted curve (3), the unknown parameter k_s was calculated to be 0.21 y^{-1} (**Figure 2**). Although the model (3) is simplified representation of the real situation, the fit is reasonably good, the coefficient of correlation between experimental and predicted data being 0.92. The mean residence time of ^{90}Sr in the reservoir consisting of surface and intermediate sea water layers being the reciprocal value of k_s was estimated to be approximately 4.75 years. This value is comparable to the result of approximately 5 years, obtained by studying water flows of the Adriatic sea water through the strait of Otranto.

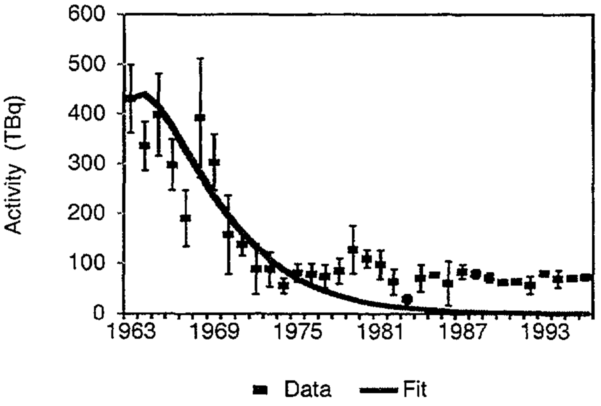

FIG. 2. Fitting the total activity data.

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HISTORY OF MERCURY MIGRATION FROM MINAMATA BAY TO THE YATSUSHIRO SEA- THE BEGINNING OF THE MIGRATION, EFFECT OF RECLAMATION AND RECENT TENDENCY

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XA9952025

We investigated migration of mercury (Hg) from Minamata Bay, the site of major methyl mercury poisoning, to the adjacent Yatsushiro Sea (636 km^2) since 1975 [1] through annual sampling of bed sediment at 26 stations. Mercury in the sediment samples was analyzed by atomic absorption spectrometry up to 1989 and by inductively coupled plasma-mass spectrometry after 1990. In 1997, we obtained historical records of mercury discharge before 1975 by analysis of sediment cores at our annual sampling stations No.1 and 4 (within 10 km distance Minamata). The results obtained from station 1 are mainly discussed in this report.

Variation in Hg concentration measured in annual sampling could not be the same with that in the core because there was some error in locating each sampling station (±100 m between 1975 and 1985, and ±10 m after 1986). Nevertheless, the depth vs. Hg concentration profile in the sediment core from station 1 was similar to the profile of year vs. Hg concentration observed at the same station (Fig. 1): both exhibited relatively constant concentrations in the shallow (recent) layers with a sharp increase in the Hg concentration in deeper (older) layers (Fig. 1). We therefore fitted the two profiles to estimate the age of each sediment layer. The 0-4 g/cm^2 layer of the core at st. 1 was fitted to 1989-1997. The concentration peak in 6 g/cm^2 layer in the core was fitted to a peak around 1986-1989 in the annual sampling profile. A concentration peak in a 10 g/cm^2 layer of the core probably falls within in the 1978-1985 period during which sampling was not conducted at this station. Age dating of each sediment layer by radioactive Pb-210 may give more precise data in future investigations.

The core probably contained a chronological record before Hg deposition started at that site because Hg concentrations at the bottom of the core, 0.1 ppm, was within background Hg concentration variation in sediments from Japanese coastal area (0.1 - 0.3 ppm). Mercury deposition at station 1 started to increase in the late 1960s and the deposition reached the maximum in the 1980s (Fig.1). Discharge of Hg with wastewater into Minamata Bay started in 1932 and stopped in 1968. The observed maximum in the 1980s was probably related to dredging of the polluted sediment in Minamata Bay conducted from 1984 to 1987.

At stations 1 and 4, Hg concentrations in the shallow layer of cores were the same as those observed in our annual sampling in the 1990s (Figs.1 and 2). However, the concentrations in the deep (5 to 15 g/cm^2) layers of core were respectively 50 % and 10 % of those observed in the 1980s at stations 1 and 4 (Figs. 1 and 2). The cause of such differences is not known.

Mercury concentrations in the Yatsushiro Sea sediment remained relatively constant the recent five years in contrast to significant concentration variation in the 1980s (Fig. 3). The observed steady state was probably caused by continuing Hg migration from Minamata though this is much decreased compared to that in the 1980s, otherwise Hg concentration would have been decreased with accumulation of fresh sediment on the surface. Desorption and upward translocation of Hg from the deep sediment layers to the sediment surface may also explain this phenomenon.

We also analyzed lead in sediment specimens from our sampling stations and found that the lead concentration decreased with distance from Minamata (Fig. 4). Lead probably was contained in sediment from Minamata Bay along with other metals such as Hg, selenium, copper and arsenic, which allegedly had been discharged into the Bay in the past.

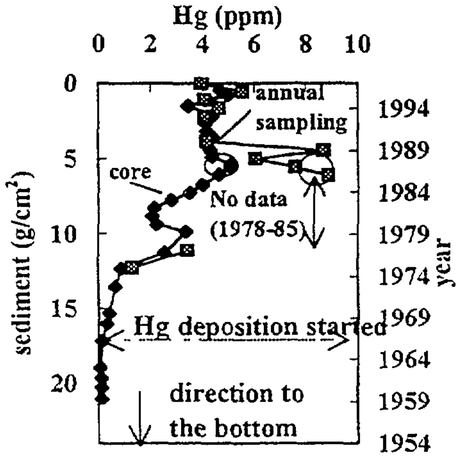

FIG. 1. Hg concentrations at Station 1.

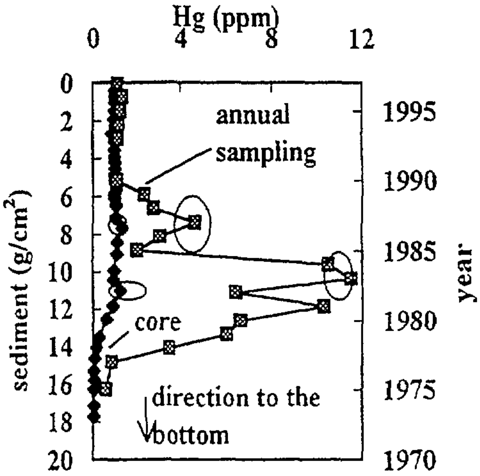

FIG. 2. Hg concentrations at Station 4.

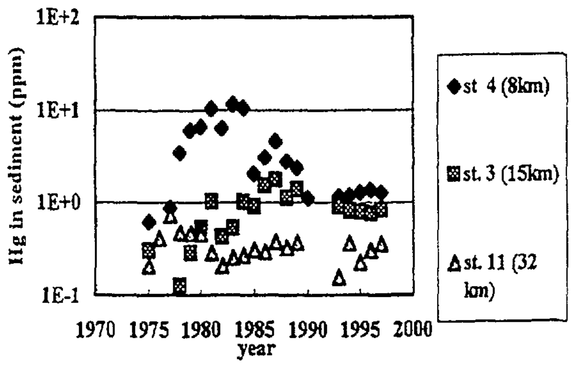

FIG. 3 Variation of Hg concentration in sediment with time at various distance from Minamata

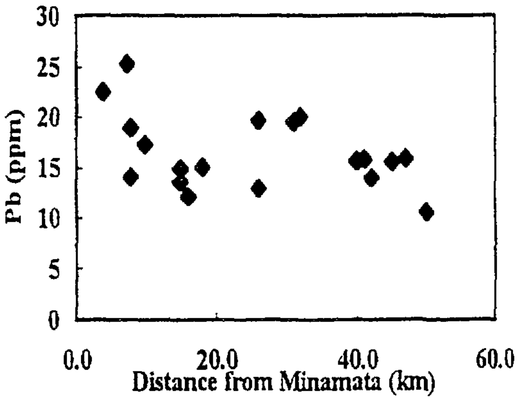

FIG. 4. Lead concentration (average of 1994-96) in sediment vs. distance from Minamata.

Our study showed that migration of Hg from Minamata Bay to the adjacent sea was relatively slow. For example, deposition of Hg at Station 1, which is located only 3.9km from the waste water outlet, started in the late 1960's which is approximately 30 years after the first discharge into the bay (1932). Such slow migration may have contributed to the localization of Hg pollution in the Minamata Bay and subsequent accumulation of Hg in the biota there.

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GLOBAL MARINE RADIOACTIVITY DATABASE (GLOMARD)

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In response to the request of Member States and under the IAEA's mandate, the IAEA Marine Environment Laboratory (MEL) in Monaco has established and maintains a Global Marine Radioactivity Database (GLOMARD).

It is a vast project compiling radionuclide measurements taken in the marine environment. It consists of systematic input of all radionuclide concentration data available for sea water, sediment, biota and suspended matter.

The GLOMARD is therefore a powerful tool for the researchers of MEL as it integrates the results of analyses in most of the areas of the marine environment which have been investigated.

The database serves the following important functions :

- Provides a snap-shot of activities at any time, which may used as a baseline for any impact assessment studies,
- Provides immediate and up-to-date information on the levels of radioactivity in the world's seas in different environmental matrices,
- Permits investigation of temporal trends in environmental levels of radionuclides and identifies gaps in available information.

In practice, these data are analysed and used for the production of graphs representing mainly the vertical concentration of radionuclides in sediment or the geographic location of zones where radioactive pollution is present.

The latest developments in the GLOMARD concern the representation of geographical location of marine radioactive pollution, which is not an easy task. The measurements used are the results of analyses of marine samples collected during scientific cruises to different parts of a the world's seas and oceans. Therefore, in order to represent a global picture of the world's seas, a specific software interpolates isolines representing the radionuclide concentration over seas.

The software "Surfer" is used to this effect. However, MEL has recently acquired a Geographical Information System (GIS). This software, when interfaced with the GLOMARD reformed under Oracle 7, allows a greater precision in the interpolation procedures and 3D images.

The aim of the project using the GIS is to allow Member States to consult the GLOMARD via the Internet and also to create maps from the data contained in GLOMARD though the MEL website.

As part of GLOMARD, IAEA-MEL has developed a database for main anthropogenic radionuclides in marine samples collected in the NW Pacific Ocean and its marginal seas around Japan. This database is based on marine radioactivity data which were compiled by Japan Chemical Analysis Center (JCAC). The data offered from JCAC were converted and missing information was added at IAEA-MEL. Additional important data were also input into the database through a literature survey. The total number of data is now about 20,000 for all samples.

The distributions of radionuclides in surface sea water and surface layer sediment were investigated using data sets installed in the database. Evaluation of data was also carried out for the vertical profiles of radionuclide concentrations, radionuclide inventories and their isotopic activity ratios in both sea water columns and sediment cores.

Generally the concentrations of ^{90}Sr, ^{137}Cs (Fig.1) and ^{239,240}Pu in marine samples collected around Japan show a tendency to decrease year by year. The influence of the Chernobyl accident in 1986 can be observed only for ^{137}Cs in surface sea water and macro-algae. Data evaluation for the radionuclide distributions around Japan have revealed the ranges of the concentrations and the average values in surface sea water and surface layer sediment. The vertical profiles of ^{90}Sr and ^{137}Cs in sea water columns show a gradual decrease in concentration with increasing depth, contrasting with those of ^{239,240}Pu which show a subsurface maximum at depth of around 700 m. On the other hand, the concentrations of all the radionuclides in sediment cores generally tend to decrease with increasing depth. The inventories of ^{90}Sr, ^{137}Cs and ^{239,240}Pu in sea water and sediment were estimated for several periods since the beginning of the 1980's up to date. The isotopic activity ratios of the radionuclide inventories in sediment cores are quite different from those in the sea water columns, reflecting the difference in removal of the radionuclides from sea water to the bottom sediment.

Finally these data were compared with data sets obtained from the first Japanese-Korean-Russian joint expedition conducted in 1994. No significant differences can be seen between the two sets of data. The data collected and evaluated here will be input into GLOMARD to be evaluated with the GIS software.

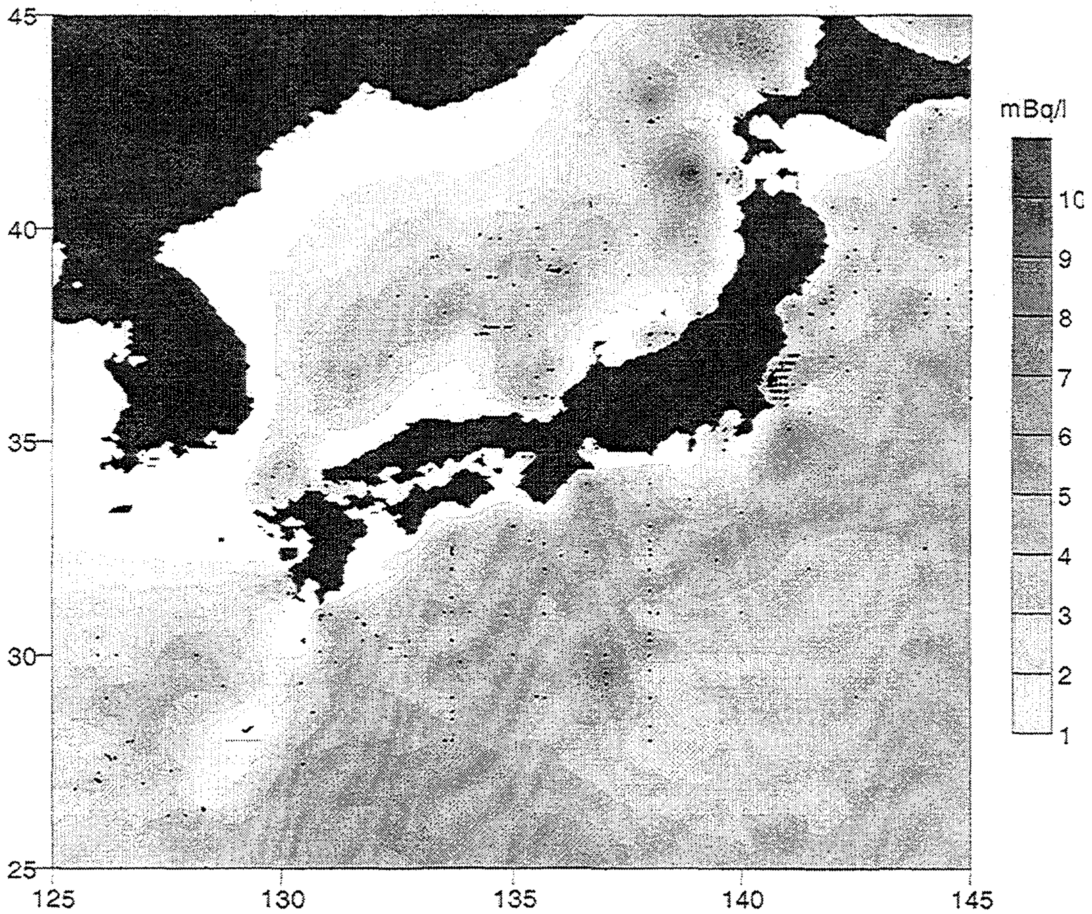

FIG. 1. The distribution of the 137-Cs concentrations in surface seawter collected around Japan (1986-1996).

IAEA-SM-354/147P

UPTAKE AND RELEASE OF ^{65}Zn AND ^{124}Sb BY *BIOMPHALARIA ALEXANDRINA AND CLEOPATRA BULIMOIDES* SNAILS AND THEIR EFFECTS ON THE ULTRASTRUCTURE OF THE HERMAPHRODITE GLAND

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The freshwater snails, are by far the most prevalent organisms among the local freshwater fauna, and represent an important group of mollusks, from the stand point of health and economy. This is due to the role played by many of them as hosts for certain parasites of man and his animals. These snails are rather considered pests and so their populations are currently controlled by several measures. On the other hand, various radioactive elements are increasingly detected in the aquatic environment, some of them may find their way to the freshwater ecosystems. So it became necessary to find any radiobioindicator from among the common aquatic biota that can be used to detect any radioactive disposal into the freshwater environment. This paper reports a radioactive tracer study on weather the previously mentioned snails can be used either in the biological treatment of low-level radioactive waste and/or as radiobio-indicators. In general, research on *B. alexandrina* is encouraged in Egypt as they serve as intermediate hosts for *Schistosoma mansoni*, a disease impairing greatly agricultural economics due to its frequent occurence among Egyptian farmers.

Cleopatra bulimodies snails are also common in Egypt, being intermediate hosts of *Prohemistomum vivax*, a parasite of dogs, cats, kites and occasionally of man. Two isotopes, namely, ^{65}Zn and ^{124}Sb were used in the present work as radiotracers.

The investigation of percent survival of *B. alexandrina* in ^{65}Zn or ^{124}Sb was performed in comparison to control snails in normal dechlorinated water and 10% sea water. It was found that about 90% of control snails in dechlorinated water were still alive after three weeks from the begining of the experiment corresponding to 100% of snails alive in 10% sea water which makes them more vital and healthy. It was found that in 20% or higher concentrations of sea water, the mortality percent increased. The survival percent of snails immersed in 3 KBq/ml ^{65}Zn after 4 weeks was found to be 60%. The corresponding value for snails immersed in 3 KBq/ml ^{124}Sb was 40% after the same period (Table 1).

TABLE I: PERCENT SURVIVAL OF B. ALEXANDRINA SNAILS IMMERSED IN DIFFERENT ACTIVITIES OF ^{65}Zn OR ^{124}Sb

Control snails			Conc. of Radioisotopes (KBq/ml)					
			^{65}Zn			^{124}Sb		
Time (weeks)	normal water	10% sea water	1	2	3	1	2	3
			% Survival					
1	100	100	100	90	80	100	90	70
2	100	100	100	90	70	90	80	60
3	90	100	90	80	60	90	70	50
4	90	90	80	70	60	70	60	40

It was found that ^{65}Zn was accumulated mainly in soft parts of the snails within which about 64% to 76% of the total amount of ^{65}Zn was accumulated in soft parts of the snails whereas the remaining amount accumulated in their shells. The uptake increased with high rate during the first three days; 17.51% and 10.79% of the initial activity of ^{65}Zn for *Biomphalaria alexandrina* and *Cleopatra bulimoides*, respectively). Then the % uptake of ^{65}Zn took place at a lower rate to reach 31.0% and 25.52% after 20 days, for the two species, respectively (Tables 2, 3). The concentration factor values increased from 8.28 after 1 day in *B. alexandrina* to reach 25.82 after 20 days. The corresponding values for *Cleopatra bulimoides* was found to increase from 3.87 after 1 day to reach 21.27 after 20 days (Figs. 1, 2).

The uptake of ^{65}Zn decreased by increasing the carrier zinc concentration to 10^{-4}M $ZnCl_2$. The concentration factor values increased to reach 19.50 and 15.23 after 20 days for *Biomphalaria alexandrina* and *Cleopatra bulimoides*, respectively, against 25.82 and 21.27 in case of absence of additional carrier in the same respective manner.

Antimony is one of the toxic elements that can be used in the control of Schistosomiazia. Thus tartar emetic, used in the treatment of this disease is potassium antimony tartarate. Results showed that ^{124}Sb has no metabolic importance, since the % uptake of ^{124}Sb increased to about 11.53% and 8.43% for *Biomphalaria alexandrina* and *Cleopatra bulimoides*, respectively after 5 days from the begining of the experiment and then remained nearly constant. The concentration factor values were found to be 9.63 and 7.03 after 20 days, in the above respective sequence.

Release of ^{65}Zn by both snails follows a biphasic curve; a fast component, through the first three days and a slow component, through the rest period. When water was used the biological half-life through the slow component was calculated and found equal to 22.5 d and 19.2 days for *B. alexandrina* and *Cleopatra bulimoides*, respectively. For EDTA the corresponding values were equal to 15.7 and 12.15d. It was found that EDTA is more effective than water as a decontaminating agent.

Release of ^{124}Sb was found to follow a monophasic curve and the biological half-lives were equal to 3.5 and 4.8 days for *Cleopatra bulimoides* and *B. alexandrina*, respectively.

Ultrastructural changes were detected (by using electron microscope) when the snails were immersed in ^{65}Zn or ^{124}Sb (1,3 KBq/ml) for 10 days. Various degrees of damage were observed. It was also found that the spermatogenetic stages are more sensitive to emmited gamma-radiations from the used radioisotopes than oogenetic stages within the same gland.

Ultrastructural section of hermaphrodite gland of *B. alexandrina* which were immersed for 10 days in 1 KBq/ml of ^{65}Zn, showed that the glycogen like granules were digested from the deposits in the middle piece of the spermatozoon tailregion.

After immersion of *B. alexandrina* snails in 3 KBq/ml ^{124}Sb for 10 days, it was found that the secondary spermatocytes suffer great damage. Accumulation of nuclear chromatine was detected.

The ova of *B. alexandrina* snails were more susceptible to gamma-rays than spermatozoa. It was also found that yolk spheres decreased in number 10 days after immersion of *B. alexandrina* in 1 KBq/ml ^{65}Zn solution. In addition primary oocytes suffer greatly from gamma radiations emmited from ^{65}Zn, while cytoplasmic matrix suffered severe degenerative changes, as shown by clearance of cytoplasm in many regions (thick arrows) and the rupture of endoplasmic reticulum (thin arrows) 10 days after immersion of *B. alexandrina* snails in 3 KBq/ml ^{65}Zn. Mature ovum of *B.alexandrina* immersed for 10 days in 3 KBq/ml ^{124}Sb showed abnormal structure of golgi apparatus (thick arrows) and digestion of yolk spheres in many regions (thin arrows).

Mature spermatozoa suffered great damage from gamma rays emitted from ^{124}Sb. Digestion of glycogenlike granules and lysis of plasma membrane were detected at many regions, 30 days after immersion of *B. alexandrina* snails in 1 KBq/ml of ^{124}Sb.

Dissection of the late spermatids and digestion of the glycogen like granules were detected 30 days after immersion of *B. alexandrina* snails in 1 KBq/ml of ^{65}Zn.

Since *Biomphalaria alexandrina* and *Cleopatra bulimoides* gastropod snails could tolerate ^{65}Zn to a considerable extent, and since they could sorb and release certain radioisotopes to a considerable extent mainly by their soft parts, they can be used either as radiobioindicators or for the biological decontamination of low-level radioactive waste. The presence of sea water upto 10% increases the survival of *B. alexandrina* snails, while higher sea water ratios decreases their survival.

ALIPHATIC HYDROCARBONS AND HOPANES AS BIOMARKERS OF THE PAST 120 YEARS SEDIMENT INPUTS IN A CORAL REEF LAGOON (TAHITI, FRENCH POLYNESIA)

XA9952028

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The study of sedimentary non-aromatic hydrocarbons (NAH) has been frequently used to determine of natural organic matter inputs, since a large fraction of these compounds derives from terrestrial and marine biological sources [1]. In addition, hopanes have been largely associated with petrochemical contamination [2].

Sediment cores were sampled in four sites in the coral reef lagoon surrounding the city of Papeete, Tahiti , French Polynesia. Sediment cores were dated by mean of ^{210}Pb activity counting in order to reconstruct past trends in environmental changes. This paper focuses on the historical evolution of NAH and hopanes in a sediment core sampled in the harbour which yielded results over a period covering 120 years. Geochronoly results evidenced a large increase in sedimentation rates from 0.33 $g.cm^{-2}.y^{-1}$ to 1.33 $g.cm^{-2}.y^{-1}$ since 1967 ± 4 y [3,4].

Total *n*-alkanes with carbon chain lenghts from C_{14} to C_{35} increased from 0,4 $\mu g.g^{-1}$ in the bottom of the core (dated 1880) to 1,7 $\mu g.g^{-1}$ in the top of the core (fig. 1). When considering carbon chain number it is possible to distinguish between marine and terrestrial inputs. Marine contribution (ΣC_{16}-C_{20}) stayed approximately constant over the whole 120 y considered period, concentrations ranging from 0.02 to 0.09 $\mu g.g^{-1}$. Contribution from terrestrial higher plant n-alkanes was assessed by the sum of long and odd numbered carbon chains (Σodd C_{27}-C_{33}). Concentrations increased from 0.1 $\mu g.g^{-1}$ in the bottom of the core to 0.65 $\mu g.g^{-1}$ in recent sediment layers.

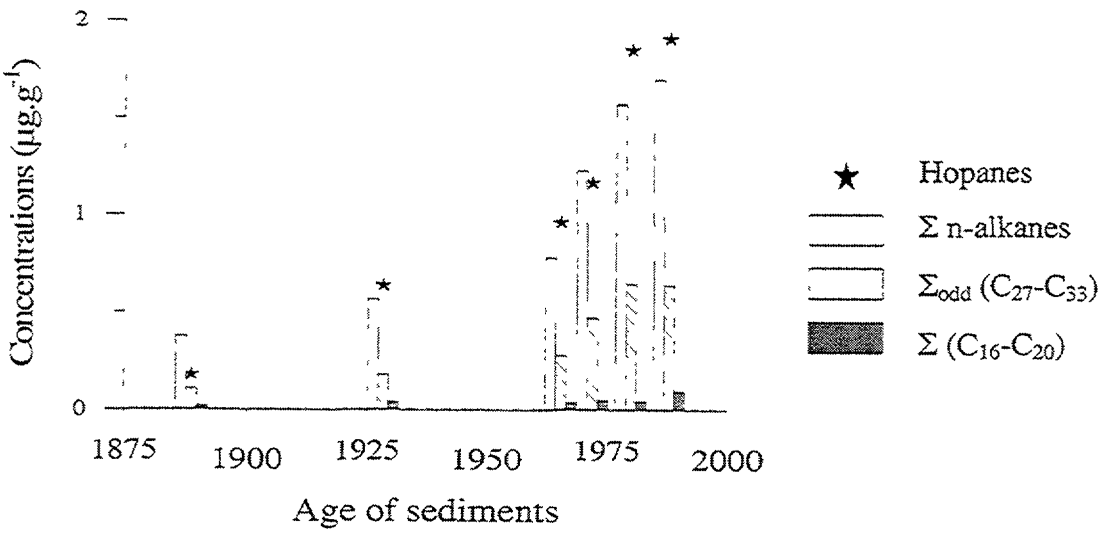

FIG 1: n-alkane et hopane concentrations relative to sediment age in Papeete Harbour.

Hopane compounds ranged from C_{27} to C_{35} and only 17α(H), 21β(H) configuration was found in our samples. The presence of 22S and 22R epimers was detected in the C_{31}-C_{35} 17α(H), 21β(H) extended hopanes. Homohopanes index, determined by the ratio between the two epimers (22S/ (22S + 22R), ranged from 0.50 to 0.65. These values were close to the equilibrium value at maturity (0.6, [5]). Total hopanes concentrations increased from 0.15 to 1.8 $\mu g.g^{-1}$ from the beginning to the end of the century (fig 1).

Concentrations in terrestrial n-alkanes and hopanes showed a very high correlation (fig. 2) suggesting that hopane compounds derived from terrestrial (natural) inputs. This point was confirmed by the good correlation with iron or manganese derived from terrestrial inputs [6]. Enrichment factors for both classes of compounds from 1880 to present days were very similar in the sediment core (between 20-25).

The flux of terrestrial n-alkanes in recent sediment layers (deposited during the past decades) was 0.85 $\mu g.cm^{-2}.y^{-1}$, while the flux of hopanes was about 3 times greater during the same time (2.45 $\mu g.cm^{-2}.y^{-1}$). These results are consistent with previous data showing an increased in terrestrial inputs since 1967 [7].

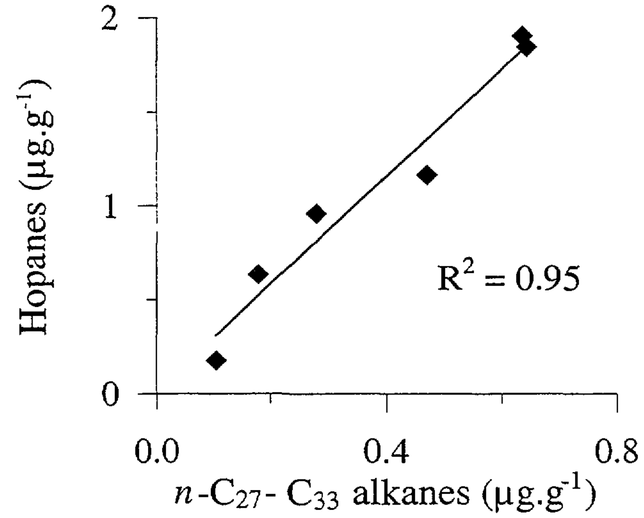

FIG. 2. Relationship between n-C_{27}–C_{33} alkane and hopane concentrations from the sediment core in Papeete harbour.

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ORGANOTINS AND OSMOREGULATION: QUANTIFYING THE EFFECTS ON THE EUROPEAN FLOUNDER *PLATICHTHYS FLESUS*

XA9952029

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The fish were kept on sediment containing 150 ng TBT.g^{-1} dry weight, in 25 l polyethylene buckets, covered with aerated seawater (35 ‰) at a constant temperature of 13 C (+/- 1 C) and maintained in a 12 hour light/dark regime. Water samples were taken on day 3 after "spiking" and the removed water replaced from a storage tank kept at 13 C. Sediment samples were taken on day 0 and day 4 after spiking. Water and Sediment samples were subsequently taken every other week. Results of a preliminary experiment showed that during the 6 week experimental period, degradation of TBT was minimal. Fish were fed once a day with frozen tubificid worms and sampled once a week for Sodium flux measurements.

We measured TBT concentrations in Upper Itchen Estuary (Southampton) sediments ranging from 70 to 170 ng.g^{-1} dry weight. Therefore, TBTCl in glacial acetic acid was adsorbed onto a dried sediment aliquot and then mixed into the sediment slurry (silver sand mixed with mud) in the bucket in order to mimic environmental concentrations (150 ng.g^{-1} dry weight; 0.4 % organic content). A sediment sample was taken for subsequent TBT analysis (t_0).

Sediments were analyzed at the Centre for Environment Fisheries and Aquacultural Science (CEFAS), Burnham on Crouch, by Gas Chromatography with Flame Photometric Detection (GC-FDP), following the procedure by [4].

Fish were blotted dry, weighed and loaded (activity of medium 653.2 Bq - 15.9 kBq) for approx. 30 minutes. The animals were then removed from the medium, rinsed and counted in a PANAX well γ-scintillation counter [1].

Fish were injected intra muscularly with 2 ul of ^{22}NaCl solution (activity: 75 kBq). Fish were counted approximately every hour. The Na efflux rates were calculated as the half-time of Na exchange [1].

General experimental setup as above. Fish were sampled at 0, 3, 5 & 9 days. Gill tissue was stained with Champy-Maillet's fixative [2,3].

During repeated rapid transfer experiments (freshwater - seawater) the control group showed the expected adaptation reaction (linear regression r = 0.92). TBT-group´s response was increasingly erratic and did not show the control group´s trend (r = 0.52). Net sodium influx in relation to the initial influx rates (t_0) differed significantly between the two groups (RM-ANOVA $p < 0.01$; fig. 1a, b).

During repeated rapid transfer experiments (freshwater - seawater), the active sodium efflux rates in the control group remained fairly constant (fig. c, d). The experimental group´s active sodium efflux rates differed significantly from those of the control group (RM-ANOVA $p < 0.05$), showing a decrease of 30 % of the initial flux rate (t_0).

Rapid transfer to seawater (35 ‰) and subsequent adaptation for 10 days showed an 87 % reduction of lamellar chloride cells for the control group. The TBT-exposed group differed significantly from the control group (RM-ANOVA $p < 0.0001$). Three days after transfer to seawater the experimental group showed a reduction of 37 % and thereafter remaining constant. No significant difference between the two groups was found for interlamellar Chloride cells (RM-ANOVA $p > 0.05$).

The average size of lamellar chloride cells of the control group was reduced 5 days after transfer to seawater by about 33 %. The cell size of the experimental group differed significantly from the control group (RM-ANOVA $p < 0.01$). No significant change in size between the groups was found for interlamellar Chloride cells (RM-ANOVA $p > 0.05$).

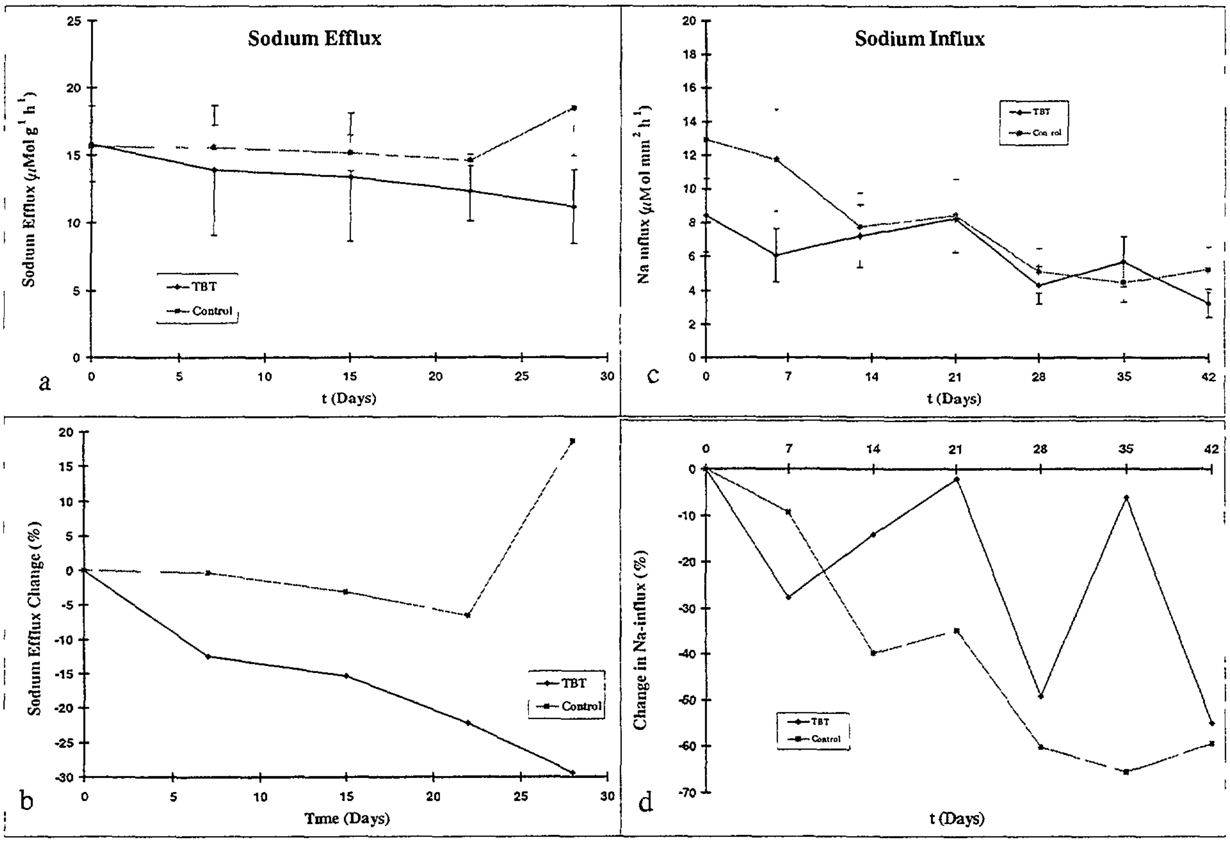

FIG. 1. Repeated rapid transfer freshwater/seawater over a period of 6 weeks. ***a)*** *Branchial sodium influx (μMol mm^{-2} h^{-1}).* ***b)*** *Change in branchial sodium influx over time in per cent initial flux rates. Branchial sodium influx. Repeated rapid transfer freshwater/seawater over a period of 28 days.* ***c)*** *Active branchial sodium efflux (μMol g^{-1} h^{-1}).* ***d)*** *Change in active branchial sodium efflux over time in per cent initial flux rates.*

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BIOGEOCHEMICAL STUDIES OF SELENIUM IN THE INDIAN OCEAN

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Selenium that is a one of trace essential elements exists mainly in the chemical form of Se(IV), Se(VI) and organic selenium in ocean. Moreover, the monitoring of the selenium species has become a matter of interest as a mean of estimating their influence in biological processes in ocean. In recent works, some investigators reported that Se(IV) shows nutrient-type especially like silica's behavior[1][2], Se(VI) shows an approximately constant value, and the biological activities control the distribution of organic selenium. However, these reports were not included the whole world's oceans. It is necessary to research several oceans for the explication of fate on selenium. We investigated at the most interesting area - the Eastern Indian Ocean where should play a key role in global ocean's cycle - for acquiring the new knowledge of selenium species at first.

High Performance Liquid Chromatography (HPLC) with fluorescence detection was used for determination of selenium in the samples. Se(IV) was fluorometric determined after extracting the complex of 2,3-diaminonaphthalene (DAN) into cyclohexane[3]. Se(VI) was first reduced to Se(VI) by adding KBr in 1.2 M hydrochloric acid solution, then the total inorganic selenium was determined by the same technique. The amount of Se(VI) was estimated by subtracting the amount of Se(IV) from the sum of Se(IV) and Se(VI). Organic selenium was determined as follows: the amount of total selenium was decomposed to inorganic ones with nitric acid and perchloric acid, and to Se(IV) by HCl and H_2O_2 was determined by the same technique. The amount of organic selenium was estimated by subtracting the amount of total inorganic selenium from the total amount of selenium.

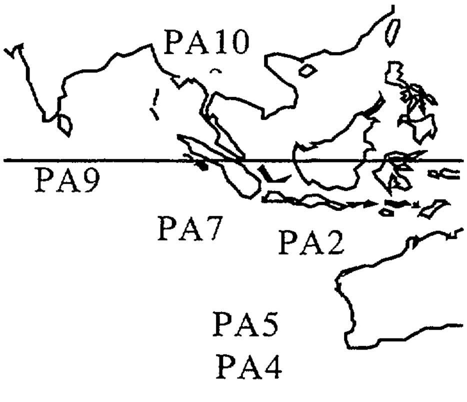

FIG.1 Sampling location

The seawater samples were collected from aboard the R/V "Hakuhou-Maru" (University of Tokyo) KH96-5 cruise at the stations PA2 (12°50'S, 117°E), PA4 (40°S, 110°E), PA5 (30°S, 110°E), PA7 (10°S, 102°E), PA9 (8°N, 89°E) and PA10 (9°52'N, 94°03'E). Our samples were collected with CTD-Carousel Multi Sampling (with 36 12-liters bottles) system. The samples were filtered through 0.45µm Membrane filters with vacuum filtration system immediately after the collection, follow by storage in a freezer (-20°C) Se(VI) and organic selenium. Se(IV) shows nutrient-type profiles of each station, and appears to have good relationships with nutrients (see Table 1). Interestingly, correlation coefficient value (r) of Se(IV) and silicate is highest of the others. This may indicate that Se(IV) and silicate have same regenerating process in ocean. The concentrations of Se(VI) are approximately constant from surface to bottom (PA2, 4, 5, 7 and 9), while the profile of PA10 shows peculiar trend that the concentration is gradually increase: the averages of 0~300m and 300m~bottom are 0.168 ± 0.010 nM and 0.786 ± 0.035 nM. The factors that are significant influence on this profile may give the following: the oxidation reaction from Se(IV) to Se(VI) or the elution of Se(VI) from bottom sediments and particulate matter from around continent.

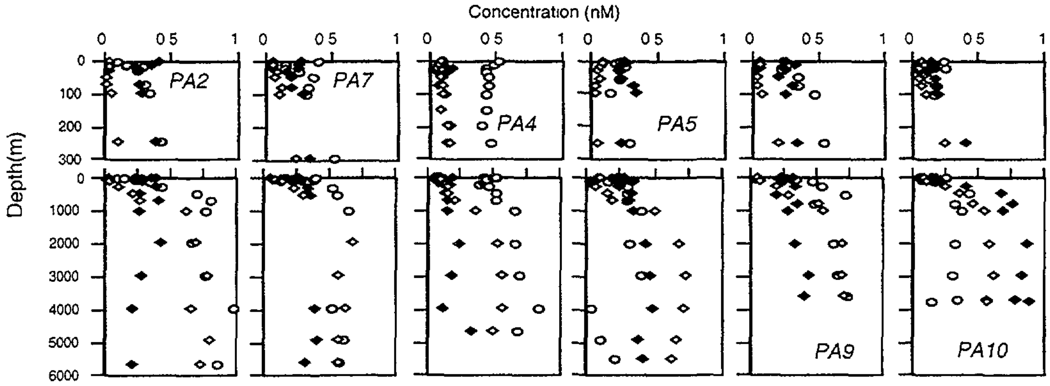

Fig 2 Vertical profiles of Se(IV), Se(VI) and Org Se in the Indian Ocean

◇ Se(IV) ◆ Se(VI) ○ Org Se

The profiles of organic selenium show two different trends. The one side, the concentrations increase slowly from surface to bottom (PA2, 7, 9 and 10). The other side, the concentrations are nearly constant of its water column (PA4 and 5). Furthermore, it appears that the correlation between the former and dissolved organic carbon is better than the latter (see Table II). This correlation indicates that each organic species in the tropics and frigid area are different substances.

TABLE I. RELATIONSHIPS OF Se(IV) (nM) VERSUS SILCATE, PHOSPHATE AND NITRATE+NITRITE(μM) IN THE INDIAN OCEAN

Zone	correlation coefficient(r)		
	SiO_2	PO_4	NO_2+NO_3
surface to bottom (n=90)	0.969	0.862	0.883
aphotic zone (n=47)	0.927	0.568	0.665

TABLE II. RELATIONSHIPS OF ORG. SE(nM) VERSUS DOC(μM) IN THE INDIAN OCEAN

Station	correlation coefficient(r)
PA2	0.969
PA7	0.866
PA4	0.395
PA5	0.105
PA9	0.933
PA10	0.585

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POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN SEAWATER FROM THE NORTHERN AEGEAN SEA, GREECE

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In this work the distribution of polycyclic aromatic hydrocarbons (PAH) in both the dissolved and particulate phases is studied in seawater from the Northern Aegean Sea (NE Mediterranean). Surface water samples (10 l volume) were collected from 15 stations during May 1997. The samples were filtered immediately through glass fibre filters (0.7 μm) in order to separate dissolved and particulate phases and were then extracted with hexane. The extracts were dried with sodium sulphate, concentrated to a final volume of 100 μl and stored frozen until analysis. Particulate matter was Soxhlet extracted for 24 h with a dichloromethane-methanol mixture (2:1). The extracts were saponified with methanolic KOH and the hydrocarbons were extracted with hexane. The hexane extracts were then cleaned up on a silica gel column and concentrated to a final volume of 100 μl. The PAH determination was performed by gas chromatography - mass spectrometry analysis (Hewlett Packard 6890 GC/MS, operating in full scan mode). The compounds identified and quantified were naphthalene and its methyl-, dimethyl- and trimethyl- derivatives, acenaphthene, acenaphthylene, fluorene, phenanthrene and its methyl- and dimethyl- derivatives, anthracene, fluoranthene, pyrene, dibenzothiophene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, perylene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.

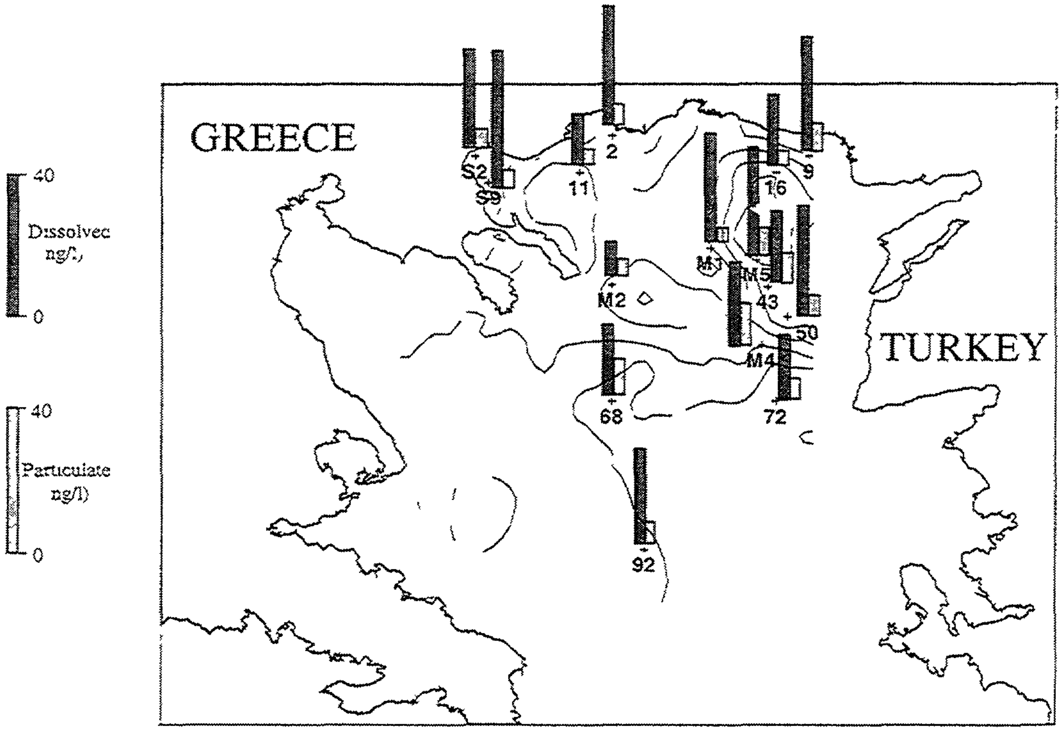

FIG. 1. Total PAH concentrations (ng/l) in surface waters from Northern Aegean Sea. Isopycnals (every 0.5, ranging from 26 to 29) at 20 dbar are also shown.

The observed PAH concentrations are displayed on a map of the region in figure 1. Total PAH concentrations (the sum of the concentrations of all the compounds determined) ranged from 9.7 to 36.2 ng/l (mean value 24.5 ng/l) in the dissolved phase and from 3.9 to 11.7 ng/l (mean value 6.3 ng/l) in the particulate phase. Data on the occurrence of PAH in seawater are scarce in the literature and there is only one reference reporting PAH values in seawater from the Eastern Mediterranean [1]. The concentrations found in this work appear to be lower than those reported in estuarine waters (Rhone delta) from the Western Mediterranean [2] but they are generally comparable with values from the North sea [3] and much higher than concentrations measured in the Cretan sea (Southern Aegean) [1]. They are considered as elevated taking in mind that most samples were collected from offshore sites.

As can be seen from figure 1 the highest values of PAH were encountered at the relatively coastal stations 2 and 9, in Strymonikos gulf (S2, S9) and at stations M1, M5 and 50 (north and east of the island of Lemnos). In order to relate the elevated values in the latter stations with the water circulation in the region, we have included the distribution of the water density at 20 meters (σ_θ) in Figure 1, as particle motion can be considered to be approximate parallel to isopycnals. The majority of low density Black-Sea water exiting the Dardanelles follows an anticyclonic route through the Lemnos-Samothraki straits and around the Samothraki (and potentially Imvros) island. The anticyclone enhances the residence time of the Black Sea water in the North Aegean, delaying its mixing with saltier Aegean water from the south.

It is noteworthy that PAH in dissolved phase were considerably more abundant than the corresponding particulate levels (dissolved PAH represented 66-88% of the total amount of PAH). This fact implies that the dissolved phase (defined by filtration on a 0.7 μm filter) play a significant role in the transport and flux of PAH as well as in their bioavailability and ultimate fate.

Regarding the compositional patterns of PAH, the dicyclic naphthalenes and the tricyclic phenanthrenes predominated in both the dissolved and particulate phases with concentrations accounting for the 70-91% of the total PAH, while PAH with 5 and 6 aromatic rings presented very low concentrations and in many samples were not detectable. This feature suggests a major petroleum origin for the PAH determined in this study. On the contrary PAH originated from pyrolytic/combustion processes and transferred into the marine environment by coastal runoff and by direct or wet deposition from the atmosphere present a predominance of five-membered ring compounds, which is not observed in our samples.

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SPECIFIC ACCUMULATION OF IODINE BY THE OPERCULUM OF THE STRAWBERRY CONCH *STROMBUS LUHUANUS*

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Accumulators having a special ability to concentrate a specific element at a high level have been discovered in the animal kingdom [1-5]. They are regarded as very effective indicator organisms for monitoring marine pollution by heavy metals and radionuclides. Since little data on the concentrations of iodine in gastropods were reported, a screening study for finding iodine accumulators was focused on gastropods.

Thirty species of gastropods belonging to Strombidae, Trochidae, Potamididae, Muricidae, Conidae and Turbinidae were collected from the shallow water of the south area of Japan from August in 1994 to September in 1995 and were dissected into several organs such as the operculum, foot, gills and intestine. Determinations of iodine in specimens were carried out by neutron activation analysis (NAA). Specimens and a standard were irradiated with thermal neutrons having 5.5 x 10^{13} n□cm^{-2}□s^{-1} of JRR-3M at the Japan Atomic Energy Research Institute. The Leco model 932 CHNS analyzer was used to measure the concentrations of C, H, N, O, and S in the operculum of *Strombus luhuanus* (FIG. 1). Point (beam size=10.m) analyses by the JEOL JXA-8900R electron probe X-ray microanalyzer (EPMA) were performed for ten targets in the operculum of *S. luhuanus* to obtain the average concentrations of Br, Ca, and Cl. The BIO-RAD Digilab FTS-60A/896 Fourier transform infrared (FT-IR) spectrometer was used to know the major component in the operculum of *S. luhuanus*. The operculum of *S. luhuanus* was digested (experimental conditions; 37., 72 hr) by a continuous treatment of an acid protease from *Aspergillus niger*, an alkaline protease from *Bacillus subtilis* and carboxylpeptidase from a bovine pancreas. Secondly, a VG Plasma Quad PQ-2 inductively coupled plasma mass spectrometer was used to select only iodine-containing fraction from many peaks which were obtained by the application of HPLC equipped with an silica-ODS column to the protease-digested solution.

The concentrations of iodine in various organs of thirty species except the operculum of the conch ranged from 0. 20 to 35.3.g/g on a dry weight basis. In contrast, the operculum of the conch have very high concentrations of iodine, as shown in TABLE.. In particular, *S. luhuanus* showed the highest concentration (mean±SD=22,800±5,200.g/g dry wt, n=10) of iodine among four species of Strombidae. The specific accumulation of iodine was thought to be common and limited to Strombidae since gastropods belonging to other families show the low concentrations (15-980.g/g dry wt) of iodine in their operculum.

Quantitative analyses by NAA or with the CHNS analyzer and EPMA revealed that the major elements in the operculum of *S . luhuanus* were : Br (..7%), C (47.7%), Ca (0.30%), Cl (1.5%), H (6.2%), I (2.3%), N (15.6%), O (16.0%), and S (0.30%). The large percentages (85.5%) of C, H, N, and O indicated that the operculum was made of organic materials. The operculum of *S. luhuanus* was mainly composed of protein since three characteristic absorption bands (amide I band at 1638 cm^{-1}. amide II band at 1517 cm^{-1}. and amide III band at 1236 cm^{-1}) indicating the presence of protein were observed from the result of FT-IR. Eleven kinds of amino acids were present in the iodine-containing fraction which was selected from protease-digested solution. In contrast, aminosugar, saccharides and lipid were not detected in it. LC/MS/MS revealed that iodine was not bonded to valine, although only valine existed as a free amino acid. It was also found from X-ray absorption fine structure analysis by synchrotron radiation that iodine atoms were covalently bonded to carbon atoms and iodine did not exist as I^2, I^- and $I0^{3-}$. From these results, we thought that iodine atoms were directly related to certain amino acids in the operculum.

FIG.1. Photograph of S. luhunaus. Its operculum (arrow) has a brown blade with saw-like teeth. Scale bar=1 cm

TABLE I. CONCENTRATIONS (μg/g DRY WT) OF IODINE IN THE OPERCULUM OF THE FAMILY STROMBIDAE

Species	Concentration	No.
Strombus luhuanus	22,800±5,200	10
Lambis truncata	5,760±1,580	5
Lambis lambis	3,680±1,200	5
Harpargo chiragra	3,630±1,000	5

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AMS MEASUREMENT OF ^{36}Cl, ^{129}I AND ^{14}C IN WATERS FROM MURUROA AND FANGATAUFA ATOLLS

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XA9952033

As part of the IAEA study of the radiological status of the marine environment at Mururoa and Fangataufa Atolls, we have measured ^{36}Cl, ^{129}I and ^{14}C in waters by Accelerator Mass Spectrometry (AMS). These measurements were carried out on samples collected by the IAEA team in July 1996. Samples included ocean and lagoon waters and underground waters from boreholes. Two of the underground waters were obtained from the cavities produced by atomic bomb tests.

The sensitivity achievable by using AMS [1] corresponds to about 10^6 atoms. Isotopic ratios are measurable to the level of 10^{-15}. Such low ratios occur in natural samples for certain long-lived radioisotopes such as ^{36}Cl and ^{14}C. Monitoring of AMS determined radionuclides in the underground environment can provide supplementary information to assist in the development and validation of geosphere transport models. Moreover, ^{129}I and ^{36}Cl, being very long-lived non-sorbing radionuclides, can be monitored over periods well beyond the half-life of ^{3}H.

All samples were prepared at ANSTO. Based on results of tritium analysis the underground and surface waters were expected to have concentrations of ^{129}I, ^{36}Cl and ^{14}C ranging over 8 orders of magnitude. The dynamic range of AMS is limited by ion source memory effects to 3 or 4 orders of magnitude. Hence a series of careful dilutions were required to ensure the isotopic ratios of the resulting samples were within the range acceptable for AMS measurement. Samples that were expected to have too high an activity level were diluted using radioisotope-free carrier solutions. Our laboratory normally deals with these radioisotopes only at naturally occurring levels, so it was necessary to be very conservative in the magnitude of dilution. In many cases, samples were over-diluted initially and had to be repeated at reduced dilution to obtain results.

Iodine – Samples were prepared by concentration of iodine from seawater using anion exchange chromatography. The iodine was purified by repeated extraction into chloroform then back extraction into sulfurous acid solution and precipitated as silver iodide. The silver iodide was mixed with equal quantities of Nb powder for AMS measurement.

Chlorine - Chloride from 2mL of seawater was precipitated as silver chloride and purified by removal of sulfates by precipitation of barium sulfate. The chloride was reprecipitated as silver chloride and loaded into sample holders lined with silver bromide.

Carbon – Carbon present in the waters as dissolved inorganic carbon (DIC) was extracted by sparging 250mL of the acidified water with He gas. The carbon dioxide was reduced to graphite and loaded in sample holders for measurement.

Table I summarises the major parameters of the AMS system used at ANSTO for these measurements, and the minimum detection limits achieved.

Table II compares the concentration of the AMS-determined radionuclides, ^{36}Cl, ^{129}I and ^{14}C, with other radionuclides analysed by conventional methods by IAEA's Marine Environmental Laboratory in Monaco [2]. As expected, the concentrations are highest in the two test cavities. The water samples from the monitoring wells contain varying concentrations of radionuclides. The concentrations of ^{14}C were much lower than expected which could be due to a number of processes

TABLE I. AMS MEASUREMENT PARAMETERS

	Accelerator voltage (MV)	Charge state analysed	Terminal stripper	Detector system	Min Detection Limit
^{129}I	3.6	5+	Ar gas	Silicon	0.05 μBq/L
^{36}Cl	7.8	7+	C foil	Gas – BCS*	1 mBq/L
^{14}C	5.2	4+	Ar gas	Gas – BCS*	10 μBq/L

*BCS = Bragg curve spectroscopy detector

occurring in the test cavity; formation of methane and carbon monoxide rather than carbon dioxide during the explosion and/or precipitation of ^{14}C as a carbonate.

In general, there is reasonable correlation between the concentrations of ^{3}H, ^{90}Sr and ^{137}Cs and those for ^{36}Cl and ^{129}I. However, some differences in behaviour are discernible because of differences in origins of the radionuclides (^{90}Sr, ^{137}Cs and ^{129}I are all fission products, ^{3}H is a fuel component and ^{36}Cl is an activation product), their sorption characteristics (^{137}Cs and ^{90}Sr are both retarded relative to the groundwater flow) and their half-lives.

The full results of the study are published in the IAEA Technical Report on Geosphere Transport [2].

TABLE II. CONCENTRATIONS OF RADIONUCLIDES IN A SELECTION OF FILTERED WATER SAMPLES (mBq/L)

Location	Site	^{3}H	^{90}Sr	^{137}Cs	^{36}Cl	^{129}I	^{14}C
Test Cavities	Aristee	$6.1\text{x}10^{9}$	$3.2\text{x}10^{5}$	$1.0\text{x}10^{5}$	3000	45	<50
	Ceto	$2.2\text{x}10^{10}$	$2.5\text{x}10^{5}$	$1.1\text{x}10^{4}$	31000	17	1280
Mururoa Carbonate Waters	Geo 10	$7.5\text{x}10^{6}$	16000	11000	19	$1.1\text{x}10^{-2}$	52
	Pieuvre 37	$8.5\text{x}10^{6}$	12000	9700	1.7	$1.2\text{x}10^{-2}$	<32
	Geo 8	$1.4\text{x}10^{6}$	1600	1100	5.4	$4.3\text{x}10^{-3}$	<32
	Tazard 14	$6.9\text{x}10^{6}$	53	78	3	$3\text{x}10^{-2}$	na
	Murene 16	$1.0\text{x}10^{7}$	103	<2	15	$1.5\text{x}10^{-2}$	na
	Isurus 10	$4.8\text{x}10^{5}$	64	12	<1	$9.4\text{x}10^{-4}$	<32
	Geo 5	$1.8\text{x}10^{4}$	8.4	20	<25	$<5\text{x}10^{-5}$	4.4
Fangataufa Carbonate Waters	Fuseau 30	$3.4\text{x}10^{6}$	340	127	3.1	$1.0\text{x}10^{-2}$	<32
	Mitre 27	$1.0\text{x}10^{4}$	2.2	20	<6	$<5\text{x}10^{-5}$	12

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IAEA-SM-354/158P

RADIOCAESIUM IN *FUCUS VESICULOSIS* ALONG THE SWEDISH COAST BETWEEN 1986 – 1995

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The Chernobyl accident in April 1986 caused an extensive radiocaesium fallout over the Baltic Sea and its drainage area. The highest fallout activities were recorded in the northern Baltic Sea at Ålands Sea. To monitor the contamination pattern, seaweed *Fucus vesiculosis* were collected at some 30 stations along the Swedish Baltic Sea coast in the summer 1986 (Figure 1). This sampling was then repeated in 1987, 1991 and 1995. In the last years around 10 stations at the Swedish west coast was included in the sampling area. At every third or fourth station also sea water was collected for ^{134}Cs and ^{137}Cs activity determination. Observed ^{137}Cs-activities in *Fucus* for the period 1986 - 1991 show an activity transport to the south and west along the Swedish Baltic Sea coast [1]. During this period almost all radiocaesium in the Baltic Sea water have been Chernobyl related. The observed activity concentration factor in *Fucus* show a negative salinity dependence.

During July 1995 a concluding *Fucus vesiculosis* and water sampling was performed. The evaluation of the preliminary results (Figure 2) support the earlier conclusions. In this paper the results of the sampling series will be evaluated and discussed. This will give information on the caesium residence time and transport in the Baltic Sea and along the Swedish west coast.

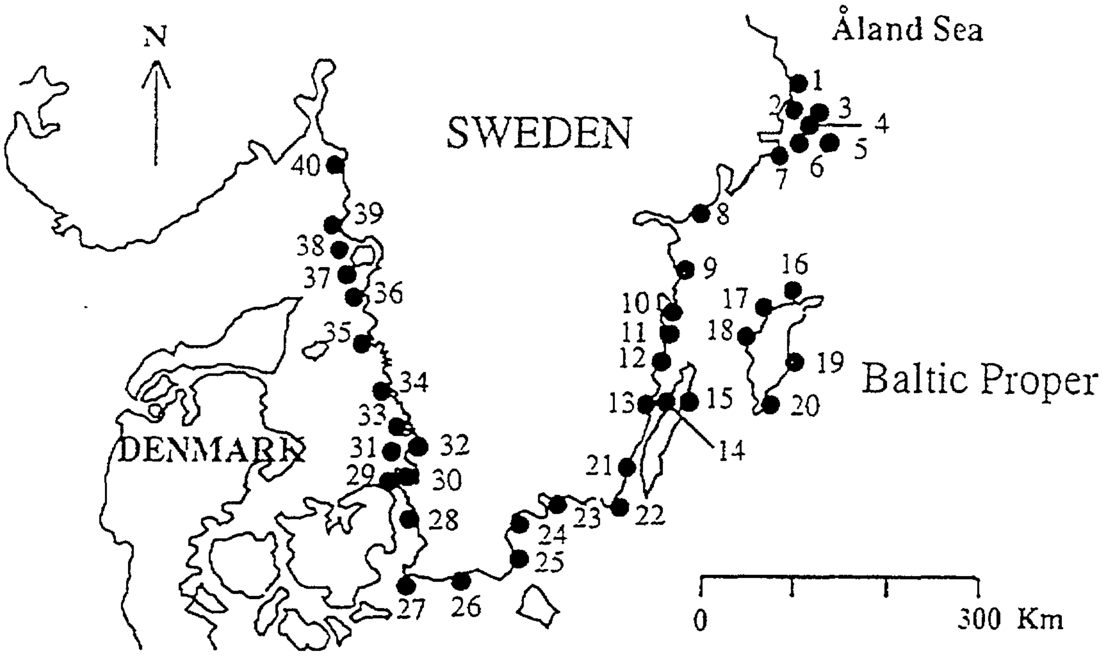

Fig. 1. Sampling Area.

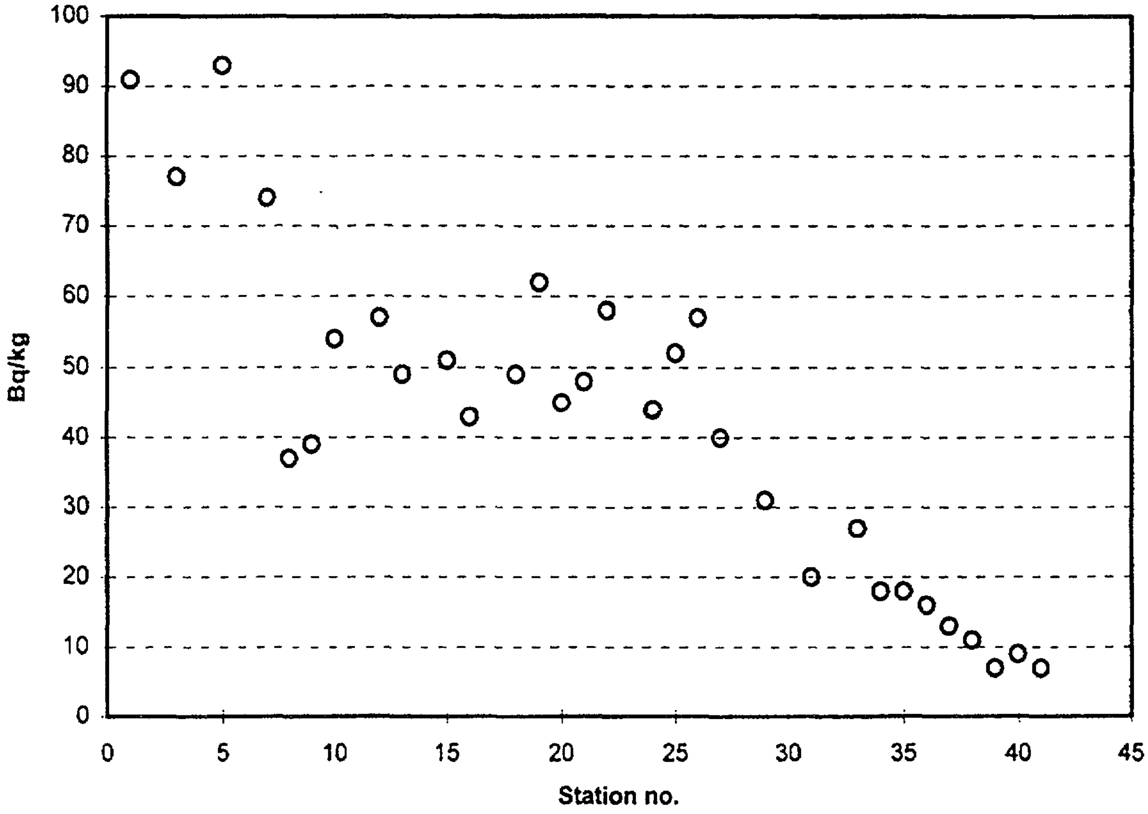

FIG. 2. Activity concentrations of ^{137}Cs in Fucus vesiculosus along the Swedish coast in 1995.

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IAEA-SM-354/159P

POLLUTION DYNAMICS AND TRACE METAL LOAD AT MAKUPA CREEK, KENYA

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XA9952035

Makupa Creek (39° 38'E, 4°2'S) was chosen as the study site due to the high anthropogenic stress excreted on it, with the aim of assessing its trace metal load, pollution source, and its sediment dynamics.

A dumping site is located on the west mainland next to the shores of the Makupa Creek. It is the only dumping site set apart for the disposal of all the towns wastes, the dumping is unregulated. The construction of the Makupa causeway, has effectively isolated the Creek from the Tudor Creek thus interfering with the water circulation dynamic this in turn causes the Makupa Creek to have pollutant sinking properties.

For comparison three sites in Mangrove ecosystems at Gazi Creek were chosen and their arithmetic mean trace metal levels obtained. Mangrove sediments are considered as pollutant sinks due to active bioturbation of sediments by crustaceans and soldier crabs [1].

Rezende (1988) and Silva (1988) have shown that mangrove sediments operate as biogeochemical sink for heavy metals, mainly due to the concentrations of organic matter and sulphides under permanently reducing conditions.

TABLE I. ARITHMETIC MEAN VALUES OF COPPER IN SEDIMENTS AT MAKUPA CREEK AND GAZI CREEK

Station	Mean dry wt (μg/g)	Standard deviation
Makupa .1	114	23.1
Makupa . 2	68.5	6.4
Makupa . 3	55.7	7.2
Makupa . 4	70.5	4.1
Makupa . 5	57.3	4.9
Gazi	6.95	0.37

TABLE II. ARITHMETIC MEAN VALUES OF CADMIUM IN SEDIMENTS AT MAKUPA CREEK AND GAZI CREEK

Station	Mean dry wt (μg/g)	Standard deviation
Makupa . 1	11.8	3.78
Makupa . 2	13	2.12
Makupa .3	11.7	2.76
Makupa . 4	10.4	1.95
Makupa . 5	10.4	1.87
Gazi	< 0.02	

TABLE III : ARITHMETIC MEAN VALUES OF IRON IN SEDIMENTS AT MAKUPA CREEK AND GAZI CREEK

Station	Mean dry wt (μg/g)	Standard deviation
Makupa . 1	22680	4461
Makupa . 2	26577	2859
Makupa . 3	25342	2355
Makupa . 4	27719	2885
Makupa . 5	25205	1067
Gazi	2653	1250

TABLE IV. ARITHMETIC MEAN VALUES OF LEAD IN SEDIMENTS AT MAKUPA CREEK AND GAZI CREEK

Station	Mean dry wt (μg/g)	Standard deviation
Makupa . 1	142.5	17.68
Makupa . 2	109.2	18.76
Makupa . 3	77.5	----
Makupa . 4	75.6	18.30
Makupa . 5	73.1	12.65
Gazi	40	14.72

TABLE V. ARITHMETIC MEAN VALUES OF ZINC IN SEDIMENTS AT MAKUPA CREEK AND GAZI CREEK

Station	Mean dry wt (μg/g)	Standard deviation
Makupa . *1*	*1429*	*156*
Makupa . 2	353	89
Makupa . 3	223	79
Makupa . 4	329	94
Makupa . 5	166	28
Gazi	13.7	1.76

Sediment samples were analysed for Cu, Cd, Fe, Pb and Zn The observed ratios for trace metals levels at Makupa Creek against Gazi Creek were:
Cu 11.1, Fe 9.6, Pb 2.5 and Zn 42.6 a clear indication of pollution, Zn having the highest relative pollution ratio.

High Cu, Pb and Zn levels 114 μg/g dry wt. 142.5μg/g dry wt and 1429μg/g dry wt respectively obtained at station 1 as opposed to levels of between 55.7 - 70.5 μg/g dry wt. for cu,73.1 - 109.2 μg/g dry wt for Pb and 166 - 353 μg/g dry wt for Zn highlights the effect of Makupa causeway on the sediment dynamics at station 1,causing it to portray pollutant sinking characteristics.
Station 2 and 4 registered similar values of Cu , Fe , and Zn , despite station 2 being next to the dumping site this is an indication that the front waters are better flushed thereby exporting the suspended contaminants away from the Creek .

Except for Fe station 5 registered low values compared to the other stations indicating that the dump site is the main source of Cd , Cu , Pb and Zn pollution.

The following observations were made:

1. The lack of proper flushing and high energy events have caused Makupa Creek to act as a pollution sink
2. Kibarani dumpsite is the main trace metal pollution source in Makupa Creek .
3. There is better flushing at the front waters than at the back waters .
4. Trace Metal levels have not exceeded the 'limit' (Cu 400ug/g , Cd 30ug/g ,and Zn 2500ug/g) proposed in a draft criteria document at an international sediment quality forum in 1982 [2].

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IAEA-SM-354/161P

DEVELOPMENT OF A SUBMERSIBLE Ge GAMMA-RAY DETECTOR SYSTEM

XA9952036

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For gamma-ray monitoring in the marine environment, a small mechanically cooled germanium gamma-ray detector system using two Stirling refrigerators has been developed. The Stirling refrigerator (Sumitomo Heavy Industry Co, Model SRS-2110) consists of a compressor (Φ60mm×120mm/1.2kg) and a cold head(Φ6.8mm×105mm/0.3kg). The compressor of helium gas is synchronized with 50 Hz of AC17V power supply. The cooling faculty of the refrigerator is I .5 W at 80K. Two cold heads of the refrigerators are connected with a Ge detector by an inverse-T type connector.

The detector system(Fig.1, Max. diving depth:500 m, Φ 188 mm×1038mm, 45 kg) consists of a detector unit and a power unit in an aluminum pressure tube. In the detector unit, there are a 100 cm^3 closed-end high-purity Ge detector with a relative detection efficiency of 21.8 % fabricated by ORTEC, a preamplifier, a main amplifier, an analog-digital converter, a high voltage controller, a temperature sensor and other electronics. The power unit operated at DC 12 V provides AC 17 V and 7 A for two refrigerators and DC 12 V for electronics.

The Ge detector is cooled to temperature of 105 K during the period of 3-4 hours. After that the temperature is automatically kept at 105 K with the DC-AC power supply using a pulse width modulation circuit and a CPU circuit for the temperature control of the Ge detector. This cooling time-consuming was similar to that of liquid nitrogen cooling. Temperature stability was +/- 0.25 K at 105 K. This stability is sufficient to prevent a peak shift and keep a good energy resolution in the gamma-ray spectrum measurements. The surface of the pressure tube was cooled to room temperature(25°C) with wet cloths and a fun, because a surface was raised to about 30°C in the air. Bias voltage of Ge detector is automatically stepped up at 105 K, and the voltage increases to 255 V with 1V/150msec and then to 2000 V with 1V/60msec. Values of full width half maximum(FWHM) energy resolution for 1.33 MeV gamma-ray of Co-60 of the detector system in and out of the pressure tube are 2.84 keV and 2.43 keV, respectively.

Sea trials of the Ge detector system have been carried out in sea areas of Rokkasho-mura where a nuclear spent fuel reprocessing facility has been under construction and Sekinehama in Aomori. The Ge detector system has been loaded onto a remotely operated vehicle (ROV, operational depth about 200 m). The total system of ROV is composed of a vehicle, a underwater cable(fiber-optic electromechanical cable of 800 m) linking the vehicle and a supporting ship, a control/navigation van, launching and recovery units and a acoustic navigation unit. The signals of two TV cameras, radioactivity data and other sensors are transmitted via the optical fiber. Although a Nal(Tl) detector system was installed in the center bottom of the original ROV, the Nal(Tl) detector system had been replaced by the Ge detector system in these sea trials. The Ge detector has been cooled to 105 K to measure gamma-rays on the deck of supporting ship before a landing on the water.

The spectral energy range of detector is about 0.1 to 3 MeV.

We could find natural decay products of U-238 and Th-232, such as Bi-214 and Tl-208, and K-40 in the spectra obtained with the Ge detector for seabed surveys of Rokkasho-mura and Sekinehama with the counting time of 20-30 min. Though concentrations of Cs-137 of the seabed around Rokkasho-mura and Sekinehama have been reported 0.4-2Bq/kg, we could not find Cs-137. FWHM energy resolution in the observed gamma-ray spectra is about 4-5 keV for 1.46 MeV gamma-ray of K-40. The energy resolution of this detector is almost the same as that of a commercial Ge detector cooled by liquid nitrogen.

Consequently it is concluded that the compact mechanically-cooled Ge detector cooled by two Stirling refrigerators has sufficient performance of in-situ gamma-ray measurements in the marine environment.

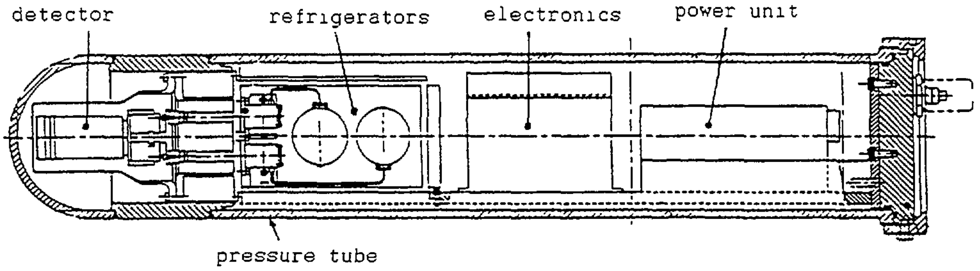

Fig.1. Schematic illustration of the submersible Ge gamma-ray detector system.

Acknowledgements

This work was supported by grants of the Science and Technology Agency of Japan and the Aomori Prefectural Government.

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IAEA-SM-354/162P

A PRELIMINARY INVEST IGATION ON THE POLLUTANT DISTRIBUTION IN THE SOUTH EASTERN BLACK SEA COAST

XA9952037

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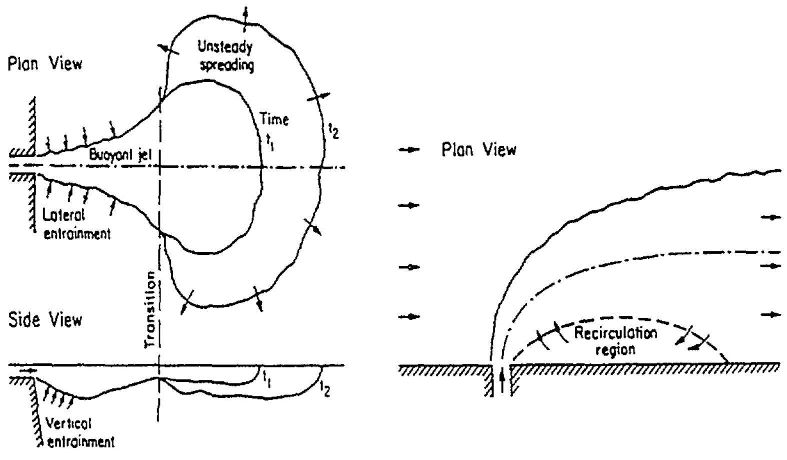
The analysis of buoyant surface jets can be simplified by recognising two separate regions: the "near-field" and "far-field" (Fig. 1). The near-field designates the extent of flow near the discharge in which the mixing is highly dependent on the discharge conditions, whereas the mixing in the far-field is dependent solely on the ambient conditions. The dilution in the near-field is highly dependent on the initial volume, momentum, and buoyancy flux of the discharge. different discharge configurations can lead to fundamentally different flow characteristic in the near-field. This forms the basis for classifying buoyant surface discharge. Four categories of near field flow patterns can be distinguished: free jets, wall jets, shoreline attached flows, and upstream intruding plumes [1]. In the near field, ambient turbulence, stratification , wind shear, and many other factors dependent on the ambient conditions play a role in determining the rate of mixing. Lateral spreading due to buoyancy and passive diffusion caused by ambient turbulence are the predominant flow processes in a majority of particle situations. Since most other processes are difficult to model and/or are generally insignificant, only buoyant spreading and passive diffusion will be considered in the far field.

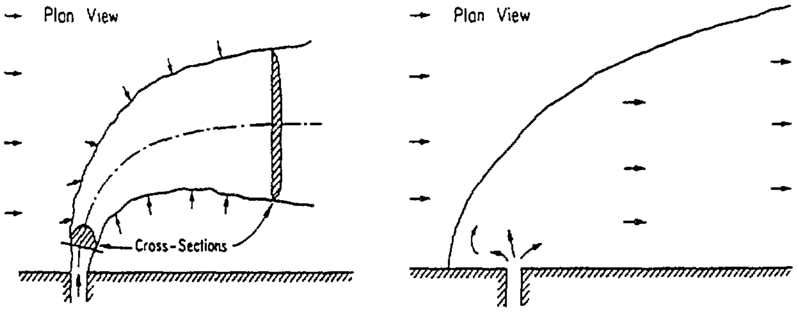
The hydrodynamic simulation is a FORTRAN program linked to the expert system through the HYDRO expert system element. It consists of a series of subroutines, each of which describes a different region of the flow. Each of these subroutines, termed "modules", is used for a region of the flow for which a particular process or processes dominate There are 17 modules which fall into four categories : The weakly deflected region, the strongly deflected region, the upstream spreading processes, and the far - field processes. A " flow protocol " refers to the specific series of modules a particular flow class uses. The relationships used to estimate the trajectory, dilution, width and depth of the in each module. Transition rules define the extent of each model. The location of the transition from one module to the next depends on both the current module and succeeding module. Discontinuities in width and depth are due to the different definitions used to describe the concentration profile. For jet like flows, the concentration profile is Gaussian and width and depth are defined to be where the concentration is 1/e (%37) of the centreline concentration. However, for flows where buoyancy - induced lateral spreading dominates, the concentration profile is assumed to be a top - hat profile, and in this case the width and depth definitions are simply- defined at the limits of the profile. For the passive diffusion region, the concentration profile is assumed to be Gaussian again, only the width and depth of flow is defined at 46%oil the centreline value, which is$(\pi / 2)1/2$ times the standard deviation. This width definition was chosen so that it matches the top- hat width definition of the buoyant spreading region while maintaining the same centreline concentration.

This study is done in the South -Eastern Black Sea region (Fig. 2). The reason to chose this area is that, fish farming is becoming important and the number of fishing cages at sea is increasing gradually. Results of *in situ* measurements are shown in Fig. 3.



a) Buoyant Surface Jet in Stagnant Ambient

c) Shoreline-Attached Surface Jet in Strong Ambient Crossflow



b) Buoyant Surface Jet in Ambient Crossflow

d) Upstream Intruding Plume in Weak Ambient Crossflow

Fig. 1. Typical buoyant surface flow patterns.

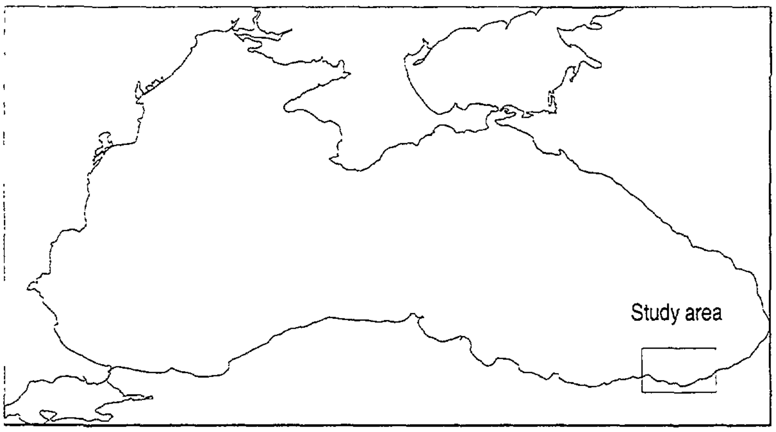


FIG. 2. Study area

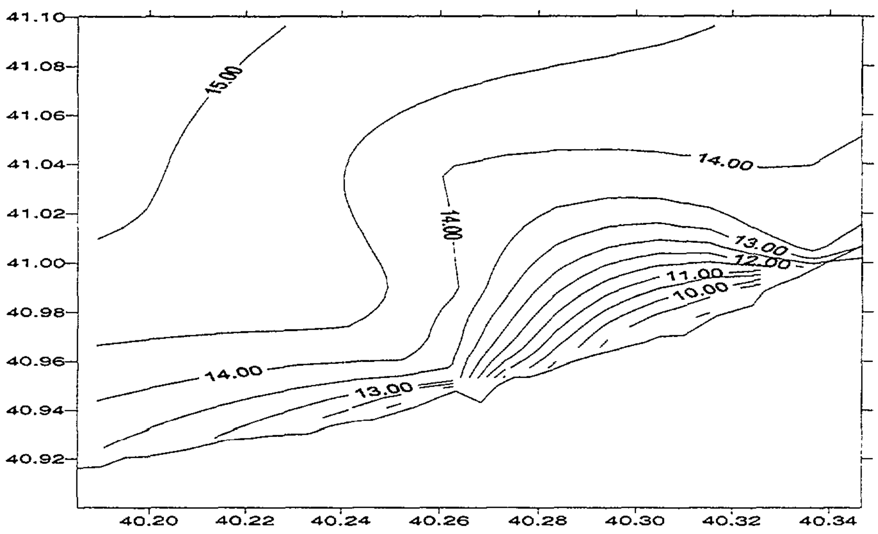


FIG 3. Results of in situ measurements (density contours of study area)

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XA9952038

IAEA-SM-354/163P

TRACE METAL CONCENTRATIONS IN MARINE ORGANISMS FROM THE EASTERN AEGEAN, TURKEY

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Monitoring of mercury, cadmium and lead levels in striped mullet (*Mullus barbatus*) was conducted in the Eastern Aegean over 3 year period and in some other species during 1996 in the framework of a National Marine Measurement Program and MED-POL II Project for the Aegean Sea. Striped mullet was recommended by [5] as monitoring species. Of all the research on the concentrations of trace metals in the Aegean environment only a little has been carried out in that part of the Eastern Aegean [9,6,2,7]. The Aegean Sea is one of the Eastern Mediterranean sub basins located between the Greek and Turkish coasts and islands of Crete and Rhodes. The study area extends from Saros Bay in the north to Fethiye in the southeastern Aegean. Heavy metal contamination of the environment has been recognized as a serious pollution problem. In particular, mercury has received much attention due to the well known toxic effects of this metal. Another element, Cd, whose toxic effects have been well documented.

Biota samples were collected by trawling from sampling stations, placed in plastic bags and stored at below -20°C until analysis. Approximately 5-7g of biota muscle was digested with 5:1 HNO_3:$HClO_4$ in microwave digestion system (Milestone Mega-1200) and diluted to the desired volume with double distilled water [3]. All the analyses were performed by Varian (Spectra AA-300 Plus) atomic absorption spectrophotometer. Mercury concentration was measured by cold vapor technique and Cd, Pb were determined by graphite furnace and background corrections were used as required. Intercalibration fish homogenate samples (obtained from IAEA, Monaco) were used as a control for the analytical methods.

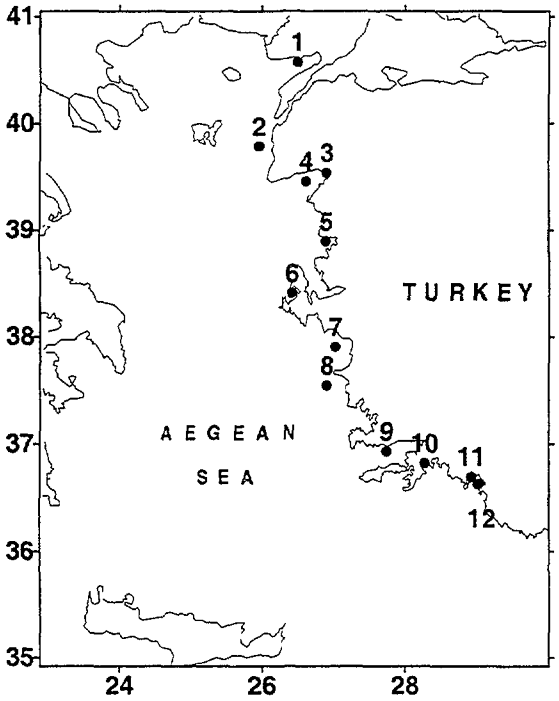

FIG 1. Map of Area

The concentrations of trace metals determined are shown in Table I, all values being expressed on a µg kg^{-1} fresh weight basis. The concentrations of trace metals found in *Mullus barbatus* varied, with Hg ranging from 17-116µg kg^{-1} fresh weight, Cd ranging from 2-12µg kg^{-1} fresh weight and Pb ranging from 85-158µg kg^{-1} fresh weight. Table 1 shows that, there is no significant seasonal variation in the trace metal concentrations. The values are similar the mean concentration of trace metals in *Mullus barbatus* from the Aegean and Mediterranean Sea [8,10,1]. Maximum concentration of Hg permitted in marine organisms are given in the majority of Mediterranean countries, ranging between 0.5-0.7µg g^{-1} fresh weight [4].

The results of Hg,Cd,Pb are presented in Table II for different species during 1996. It can be seen that levels, are similar, except for mercury and lead, where they are significantly higher in *Pagellus erythrinus*, *Citharus linguatula* for mercury values; in *Parapenaus longirostris*, *Mytilus galloprovincialis* for lead values in the Aegean Sea.

As a general conclusion, the levels of trace metals determined in the different organisms under study area considerably lower than those found in polluted area of Mediterranean Sea.

TABLE I Trace Metal Concentrations in Mullus barbatus (µg kg^{-1} fresh weight)

Sampling Date	Sampling Location	Number of sample	Length Range(mm)	Range of weight(gr)	Hg	Cd	Pb
July 1994	1	4	118-138	26-39	51	10	138
	2	10	140-160	48-63	48	10	139
	3	5	110-125	25-38	30	11	119
	4	10	140-160	50-65	25	10	146
	5	10	110-140	25-36	71	10	179
	7	10	110-140	25-37	87	9	116
	8	5	134-145	29-40	52	8	110
	9	10	106-115	21-25	23	8	122
Dec.1994	1	10	129-144	28-38	52	11	115
	3	10	118-138	24-38	17	9	116
	4	10	110-140	23-39	17	12	149
	5	10	110-140	24-38	20	11	157
	6	10	120-130	26-34	71	10	147
	7	10	118-135	28-36	51	9	116
	8	10	113-137	24-37	27	7	112
	9	10	110-130	23-35	38	8	113
May 1995	2	10	120-135	27-41	62	10	108
	3	10	124-138	28-44	16	9	115
	4	10	128-145	28-40	18	12	150
	5	12	130-155	28-65	21	10	152
	6	10	111-145	20-38	66	8	146
	7	10	120-145	26-40	27	8	109
	8	10	130-148	28-40	21	7	110
	9	10	128-145	27-39	19	8	113
June 1996	2	10	130-145	26-38	95	4	129
	4	10	128-145	29-41	84	2	138
	5	9	134-150	33-60	44	2	124
	6	10	120-140	27-35	84	3	127
	8	10	132-156	30-65	38	4	110
	9	8	135-160	36-66	74	2	158
	10	10	123-148	28-42	44	2	124
	12	10	135-150	33-59	72	2	158
Oct. 1996	1	11	110-150	22-58	69	2	158
	3	10	120-135	28-41	92	3	113
	6	24	155-200	58-96	27	2	135
	8	20	130-160	31-61	64	3	85
	9	20	140-180	39-92	116	4	153
	10	15	150-170	54-88	107	3	112

TABLE II. Trace Metal Concentrations in Biota ($\mu g\ kg^{-1}$ fresh wt.) from Eastern Aegean Sea (1996)

Sampling Location	Organism	Hg	Cd	Pb
1	*Citharus linguatula* (Spottet flounder)	900	1.6	12
	Merluccius merluccis (Hake)	39	1.0	112
	Lophius piscatorius (Angler fish)	142	1.3	89
	Parapenaus longirostris (Pink shrimp)	110	2.7	2514
	Octopus vulgaris (Octopus)	243	1.9	23
2	*Lophius piscatorius* (Angler fish)	179	1.2	122
3	*Diplodus annularis* (Annular sea bream)	225	1.4	229
	Serranus hepatus (Black comber)	180	1.0	-
	Trisopterus minutus (Poor cod)	240	1.1	13
	Merluccius merluccis (Hake)	60	1.6	64
	Octopus vulgaris (Octopus)	427	1.3	110
4	*Merluccius merluccis* (Hake)	112	1.8	124
	Pagellus erythrinus (Red pandora)	375	1.5	113
5	*Diplodus annularis* (Annular sea bream)	234	2.9	918
	Pagellus erythrinus (Red pandora)	328	1.5	142
	Merluccius merluccis (Hake)	74	1.0	78
	Lophius piscatorius (Angler fish)	324	1.7	13
	Trisopterus minutus (Poor cod)	330	1.0	68
	Citharus linguatula (Spottet flounder)	375	1.1	67
	Diplodus annularis (Annular sea bream)	441	1 0	17
	Solea vulgaris (Common sole)	170	1.0	-
	Mytilus galloprovincialis (Mussel)	54	1 5	1979
6	*Pagellus erythrinus* (Red pandora)	532	1.0	124
7	*Pagellus erythrinus* (Red pandora)	24	1.0	134
	Merluccius merluccis (Hake)	211	1.0	346
8	*Pagellus acarne* (Axillary sea bream)	347	1.0	20
10	*Pagellus acarne* (Axillary sea bream)	397	1.4	17
	Pagellus erythrinus (Red pandora)	235	1.6	27
11	*Pagellus erythrinus* (Red pandora)	154	1.1	49
12	*Pagellus acarne* (Axillary sea bream)	39	1.0	26

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IAEA-SM-354/164P

RADIOCAESIUM, PLUTONIUM AND AMERICIUM PARTITIONING AND SOLID SPECIATION IN SIZED, INTER-TIDAL SEDIMENTS FROM STRANGFORD LOUGH

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Fine-grained surface (0–2 cm) sediment was collected at an inter-tidal site (Mahee Island) in Strangford Lough, on the NE coast of Ireland in September 1997. The sediment was wet-sieved into standard sized fractions using *Endecott* test sieves and the fractions assayed for ^{137}Cs, ^{239,240}Pu and ^{241}Am content. Sub-samples of each fraction were measured with a *Malvern 2600* laser diffraction analyser, which confirmed that >90% of the particles in each fraction was in the defined size range. The mass distribution of the sediment, as determined by wet-sieving, is shown in Fig.1, together with the distribution within the <38 μm fraction, which was determined by laser diffraction.

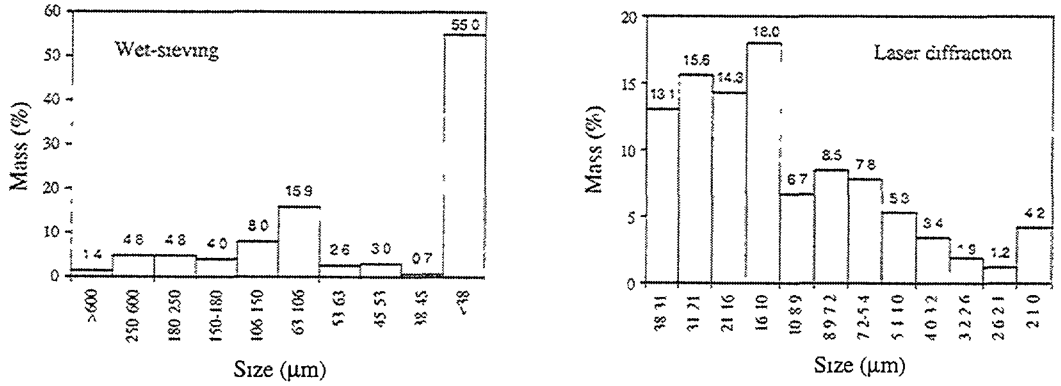

FIG. 1. Particle-size distribution in intertidal sediment from Strangford Lough.

The sediment, classed as a silt/mud, is typical of much of the material in the intertidal zone inside the lough (an observation confirmed by the particle size analysis of samples from other sites throughout the lough). About 55% of the material was in the form of particles of size <38 μm. Importantly, for each of the nuclides considered, 90–95% of the activity was associated with this fraction, with the remainder distributed across the other sized fractions (Table I). This highlights

TABLE I. ^{137}Cs, ^{239,240}Pu AND ^{241}Am ACTIVITY DISTRIBUTION IN SIZED SEDIMENTS FROM STRANGFORD LOUGH

Size fraction (μm)	**Massic activity (Bq kg^{-1}, dry wt.)** ^{137}Cs	^{239,240}Pu	^{241}Am	**% of total activity in fraction** ^{137}Cs	^{239,240}Pu	^{241}Am
250 – 600	4.8 ± 0.5	1.19 ± 0.03	1.39 ± 0.07	0.2	0.5	1.3
180 – 250	5.2 ± 0.4	1.07 ± 0.04	0.67 ± 0.04	0.2	0.4	0.6
150 – 180	7.4 ± 0.4	1.31 ± 0.04	0.83 ± 0.04	0.3	0.4	0.6
105 – 150	12.0 ± 0.5	1.66 ± 0.05	1.05 ± 0.05	0.8	1.1	1.6
63 – 105	18.4 ± 0.7	1.75 ± 0.06	1.25 ± 0.06	2.5	2.4	3.7
53 – 63	17.9 ± 0.5	2.71 ± 0.06	2.18 ± 0.08	0.4	0.6	1.1
45 – 53	21.4 ± 0.6	3.32 ± 0.07	3.68 ± 0.13	0.6	0.8	2.0
38 – 45	20.5 ± 0.5	4.76 ± 0.12	3.8 ± 0.2	0.1	0.3	0.5
<38	200.8 ± 1.2	20.1 ± 0.4	8.6 ± 0.2	94.9	93.4	88.6

the importance of defining a sized fraction when monitoring the temporal evolution of particle-reactive pollutants.

The solid phase speciation of ^{137}Cs, ^{239,240}Pu and ^{241}Am in the <38 µm sized fraction was examined using a sequential extraction protocol (Table 2) recommended by NIST [1]. The protocol, designed to determine the partitioning of trace metals into phases likely to be affected by environmental conditions [2], separates the activity into six geochemical fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, acid soluble and residual.

TABLE II. EXTRACTION SEQUENCE APPLIED TO STRANGFORD LOUGH SEDIMENT

Fraction	Extractive reagent	T (°C) ; duration	Reagent/sample ratio (ml g^{-1})
Water soluble/exchangeable	0 4M $MgCl_2$, pH 7	25°C, 1 hour	10 1
Carbonates	1M NH_4Ac, pH 4 with HAc	25 °C; 6 hours	10 1
Oxides (Fe/Mn)	0 04M NH_2OH HCl in 25% HAc, pH 2	90 °C, 6 hours	10 1
Organic matter	30% H_2O_2 in 0 02M HNO_3, pH 2	90 °C, 6 hours	10 1
Acid soluble	8M HNO_3	90 °C, 6 hours	10 1
Residual	-	-	-

The results of the solid speciation analyses are summarised in Table 3. Most of the ^{137}Cs involved (~80%) was found to be tightly bound, being associated with primary and secondary minerals within the sediment. In contrast, much of the ^{241}Am (~70%) was found to be associated with organic, oxide and carbonate phases, supporting the extensive evidence already available of the importance of these phases in the scavenging and removal of americium to seabed sediment.

TABLE III. SOLID SPECIATION OF ^{137}Cs AND ^{241}Am (± 1σ) IN THE <38 µm SEDIMENT FRACTION

Fraction	% total ^{137}Cs	% total ^{241}Am
Water soluble/exchangeable	5 ± 1	9 ± 3
Carbonates	9 ± 1	14 ± 2
Oxides (Fe/Mn)	4 ± 2	24 ± 2
Organic matter	4 ± 3	29 ± 5
Acid soluble	73 ± 5	23 ± 4
Residual	5 ± 2	1 ± 1

Acknowledgements

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AN OPERATIONAL OIL SPILL MODEL FOR THE LEVANTINE BASIN (EASTERN MEDITERRANEAN SEA)

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Accidental oil spills in the sea and in the coastal waters are a matter of great environmental concern due to their impact on various coastal resources and marine activities. The basic response to an oil spill in the marine system employs different measures and appropriate equipment to combat it. The efficiency of such marine operations depends greatly on the prediction of the movement and weathering of the oil. Such predictions are greatly enhanced by the application of numerical models to forecast :

a) where the spill will most likely move to,
b) which resources are threatened,
c) how soon it will get there and
d) what will look like when it arrives.

To fullfill the above objectives a numerical oil spill model (MEDSLIK) for the Cyprus and Levantine Basins has been developed and is currently being used at the above Laboratories of the Department of Fisheries. The MEDSLIK model incorporates the transport, fate and weathering processes of the oil. The oil is considered to consist of a light evaporative component and a heavy non evaporative component. Emulsification is also simulated, and the viscosity changes of the oil are computed according to the amounts of emusification and evaporation of the oil. The dispersion of the oil into the water column (caused by the influence of wind-induced waves), coastal impact and adhesion, transport of slick by the ambient wind and mechanical spreading are also considered.

The fate algorithms in the model are those of Mackay [1,2] which have received extensive experimental calibration in the past. The transport algorithm has been calibrated based on an analysis of observational data from the movement of drift buoys that were designed to imitate the movement of oil [3], while the spreading algorithms use a modification of the Fay formulas [4,5] that again is emperically based [6].

The MEDSLIK oil spill model requires as input data the date, time, location and duration of the spill (either the rate of spillage or the total volume of the spilt oil). The type of oil is entered either by selecting from the REMPEC database of oil characteristics or via its API number in case the oil name is unknown. The wind speed and direction at the spill site are entered either as constants for the period of simulation or as a table of values.
Sea state conditions are computed internally based on the wind field. The sea surface temperature is obtained, according to the time and location of the spill, from an included hydrological dataset of the Levantine Basin or is entered as a constant for the period of simulations.

The particles of oil in a spill are transported by the water in which or on which they are situated. In the Mediterranean Sea there are two dominant mechanisms that drive the water currents, the surface forces provided by the winds and the gravitational forces induced by variations in water density. The model incorporates a database of background 3D currents computed from a comprehensive set of temperature/salinity data measured under the CYBO project [7] combined with similar data from the MEDATLAS database [8]. Moreover, in-situ currents may entered in accordance with the available information. Within the frame of EU oceanographic projects new information on the sea water currents will included.

The model allows the user to investigate the effect of deployment of booms on the spill. This model component provides critical assistance in the decision where best to deploy booms. The model has the capabilities of incorporating its own GIS-Geographical Information System containing information on commercial fisheries activities, and industrial, recreational and environmental resources in the coastal zone of the Levantine Basin.

Several scenarios of accidental spill at different coastal sites have been simulated in the coastal sea area of Cyprus within the framework of the national contingency plan to combat accidental oil pollution in the near coastal sea areas. The application of the MEDSLIK model will, we hope, assist in the effective and timely response to future marine oil pollution accidents in the Levantine Basin that should certainly benefit all the coastal nations in the region.

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THE ACTIVITY AND THE DEVELOPMENT OF RADIOECOLOGY MARINE LABORATORY IN INDONESIA

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Indonesia marine has a big potential to be polluted due to terrestial and marine activities. For anticipating the future trend of environmental marine pollution, Indonesia has to built the Radioecology Marine Laboratory (RML). The RML that will be built must have capabilities in monitoring and doing safety assessment of the concentrations level trend, distributions, migrations and the accumulation of radionuclides in ecosystem marine. The RML to be developed also has to adopted and develop the using of nuclear techniques for understanding and to minimise the environmental impact problems. The RML is proposed to be build in the perimeter of Indonesia territorial.

The activities in the field of marine radioecology in Indonesia are spreading in many government institutions and more focused in terrestrial. In this paper, beside the RML proposed is explained also the radioecology studies at NPP candidate site of Muria Peninsula during fiscal year 1997 - 1998 are reported.

The atmospheric dispersion factor (χ/Q) for NPP candidate site was calculated using GENII packet program [1]. The calculations was done for 16 sectors and the distance up to 100 km from release point. The meteorological data (wind-rose and stability-class) of NEWJECT [2,3] reports was used and the stack height is assumed 100 m. The results of (χ/Q) calculation are shown in Figure 1 and Figure 2. The highest (χ/Q) value rate is 4.75 E-07 to 8.23E-07 second. m^{-3} in distance of 700 m from the release point for west-sector. Based on this value we are able to calculate the Derived Release Limit (DRL's) for atmospheric release in Muria Peninsula. The calculation of DRL's using site specifics data and critical pathways will be done in the fiscal year 1998-1999.

Dispersion of radionuclide (C/Co) in the coastal of Muria Peninsula was calculated using open-coast model [5]. The velocity of sea current in summer and rainy season of Muria Peninsula from NEWJECT data survey in INRPB-4 document was taken account in the calculations [6]. The coefficient diffusi lateral (Ky) was used in the interval 0.5 to 5.0 m^2. $Second^{-1}$ [8]. The ^{137}Cs (Half-life; 30 years) and ^{90}Sr (Half-life; 28,7 years) are taken in the calculation. The results are shown in the Figure 3 to Figure 6. The (C/Co) in summer season is not different significantly with the (C/Co) in rainy season, that is 4..24 to 5.86 E-07 respectively. The calculation of (C/Co) has to be recalculated with site specific data using another model for validation.

The investigations of Pu and Am isotopes contains in the Muria Peninsula marine sediment was carried out. The objectives of these investigation is to know the base level of these radionuclides before NPP operations in this site. The sampling stations are shown in Figure 7. Sediment samples were collected in 1996 at 10 site along coast of Muria Peninsula. All samples from each site were dried to a constant weight, crushed to pass 2 mm diameter sieve, carefully mixed and weighted.

For radiochemical separation and purification of plutonium and americium were used 8M HNO_3, 8M HCl, (1+9) H_2SO_4, $HClO_4$, NH_4OH, H_2O_2, thymol blue, Oxcalic acid, $(NH_4)_2C_2O_4.H_2O$, iron carrier (20 mg Fe^{3+}/Cm^3), calcium carrier (100 mg Ca^{2+}/cm^3), 0.1 M HI-8M HCl, 1M HNO_3 - 93 % CH_3OH, 0.1 M HCl-0.5M NH_4SCN-80% CH_3OH, 1.5M HCl-86% CH_3OH and anion exchange resin (Biorad chloride form 100-200 mesh and 50-100 mesh). An anion exchange resin used was purified by washing it with 3M NaOH, 6M HCl, and finally, distilled water. ^{242}Pu and ^{244}Cm used as chemical yield monitors were supplied by Amersham Radiochemical.

^{238}Pu, $^{239,240}Pu$ and ^{241}Am were determined by alpha -spectrometry subsequent to radiochemical separation and purification. Alpha spectrometry was performed using a 450 mm^2 silicon surface barrier detector (ORTEG BR-025-450-100). The resolution of α-spectra was $\leq$ 25 keV for the ^{241}Am peak (5.49 MeV). Each detector was coupled to multichannel analyzer (SEIKO EG & G 7800).

The electrodeposition cell was made of polyethylene, the internal diameter being 20 mm and the height being 82 mm. Stainless steel cathode disc (ϕ: 30 mm, thickness: 15 mm) was fixed by stainless steel holder, and platinum wire was used as anode. The distance between anode and cathode both of which were connected to DC. power supply, was about 5 mm.

The concentrations of ^{238}Pu, $^{239/240}$Pu and ^{241}Am in sediment samples were shown in Table 1. It can be seen from Table 1 that $^{239/240}$ Pu and ^{241}Am were detected in all sediments samples. Concentrations of these radionuclides were relatively high in sediment collected from number 4 - 10 sites and low at number 1 - 3 sites. The concentration of ^{238}Pu was far below those of $^{239/240}$Pu and ^{241}Am. Low concentration at 1 - 3 sites can be because of the dilution of surface sediment due to the mixing with fresh uncontaminated terrestrial materials supplied by river flowing into this location.

Concentrations level of $^{239/240}$Pu and ^{241}Am found are higher than those found in surface soil of Serpong Nuclear Research Center area. The average concentrations in surface soil of Serpong were found to be 17.03 ± 2.49 mBq/kg for $^{239/240}$Pu and 9.20 ± 2.93 mBq/kg for ^{241}Am. The high concentration in the sediment may be explained by the inflow of surface soil containing amounts of these radionuclides. Fallout radionuclides reach into the sediment through two pathways. Ones is the direct deposition of radionuclides from the atmosphere onto the surface of water and subsequent incorporation into sedimenting particles. The second is the erosion of the surface soil of the watershed and transport to the water body [10].

Concentration of $^{239/240}$Pu was also higher compared to the reported value for Antarctic area. The low concentration of fallout in the Antarctic area than Muria Peninsula may be explained by the long distance of the Antarctic which is believed to be the least contaminated area in the world because of the lowest human activity and there are no nuclear installations, the soil can be expected to contain only radionuclides deposited by worldwide fallout [11].

The concentrations of ^{238}Pu, $^{239/240}$Pu and ^{241}Am in sediment from Muria Peninsula are lower then those found in Japan [12, 13, 14], Irish sea [15], Czechoslovakia [16] and South Korea [17].

Isotopic ratios of various radionuclides frequently reflect their origin. For example, the ^{238}Pu/ ^{239,240}Pu activity ratio from nuclear fuel reprocessing plants, fresh fallout and weapon grade plutonium are in the order of 0,28, 0,026 and 0,020 respectively and can be used to identify source terms and transfer factor [9].

Activity ratio of ^{238}Pu/ ^{239,240}Pu and ^{241}Am/ ^{239,240}Pu in sediment collected from Muria Peninsula is shown in Table 2. The range activity ratios of ^{238}Pu/ ^{239,240}Pu at sites studied 0.02 - 0.04 are close to the value for lake and sea sediment in Japan [14] and soil in Bavaria [18] and Czechoslovakia [16]. The ^{241}Am/ ^{239,240}Pu activity ratio in the sediment samples from Muria Peninsula were mostly 0.3. This ratio is identical to the value of 0.32 and 0.35 reported by Yamamoto in lake and sea sediment from Japan respectively [14]. It is also identical to the reported mean of 0.3 found in soil of Bavaria in 1994 [18]. The results of the comparison of the activity ratio indicated that these radionuclides of the fallout from nuclear bomb test.

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THE RED ALGA *GRACILARIA VERRUCOSA* (HUDS.) PAPENS. AS AN INDICATOR FOR METAL POLLUTION IN THERMAIKOS GULF (GREECE)

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Thermaikos Gulf (Aegean Sea, Greece) receives pollutants from direct urban effluents (containing Cu, Zn, Fe and Ca) from the industrial zone and the sewage of 1.200.000 inhabitants of Thessaloniki city. Since 1992 only 30% of these wastes had been treated in the sewage plant. Effluents from Greek activities are also discharged into Thermaikos Gulf through 4 rivers. Axios river also transfers pollutants from Yugoslavian activities.

Seasonal samplings of the red alga G*racilaria verrucosa* (Huds.) Papens., of the sediment and seawater from three stations (Nea Krini, Biamyl, Perea) distributed along the coast of Thermaikos Gulf were made (Fig. 1). Iron, Pb, Zn, Cu and Cd concentrations in the alga and sediment after wet digestion and in the salt left after evaporation of the seawater were measured by flameless AAS (Perkin-Elmer HGA 72).

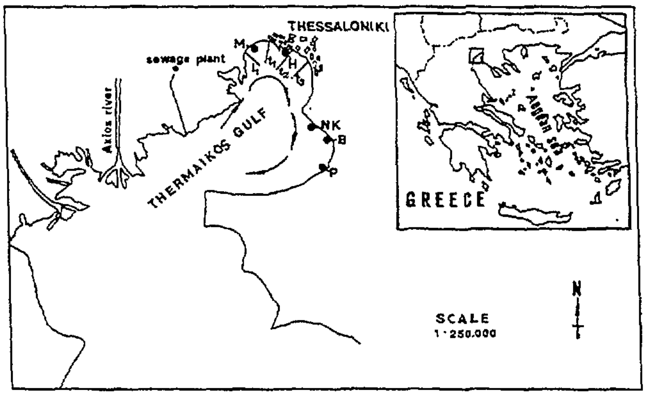

Fig. 1. Sampling stations in Thermaikos Gulf: NK=Nea Krini; B=Biamyl; P=Perea; With M is symbolized the industrial area (Mamidakis), with H the Harbour. The direction of sea currents (according to Ganoulis and Krestenitis 1982 [1]) is marked with an arrow, while the industrial (I_1) and domestic wastes (t_1, t_2, t_3) are discharged, are marked with vertical lines.

The concentrations of all metals in the alga and the seawater were distributed uniformly ($p > 0.05$) among the stations (Kruskal-Wallis analysis). Lead, Zn and Cu concentrations in the alga were higher in Biamyl station, of Fe in Nea Krini and of Cd in Perea. Lead and Cu concentrations in the sediment demonstrated significant ($p < 0.01$) local distribution; the concentrations of all metals in the sediment and of Pb in the seawater were higher in Biamyl station. There is a number of shipyards around this station while metals are likely to be transported from the industrial zone towards this station due to the direction of sea currents.

Significant seasonal variation (Kruskal-Wallis analysis) demonstrated Cd and Fe concentrations in *G. verrucosa* (Fig. 2), Zn concentrations in the sediment and Cd, Cu and Pb ones in the seawater. Copper and Fe content, in the alga increased from winter to summer, whereas those of Cd followed an opposite pattern (Fig. 2). Zinc concentrations in the plant were minimum in spring, whereas Pb ones were higher in spring (Fig. 2).

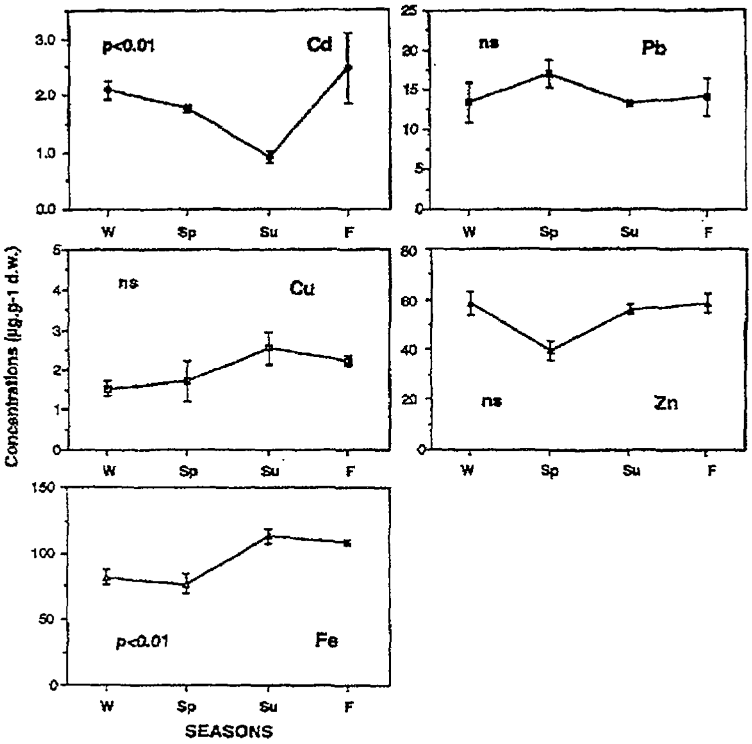

Fig. 2. Seasonal variation of metal concentrations in Gracilaria verrucosa (μg g^{-1} d.w.). Each dot represents the mean of the values recoreded in a season at all sampling stations; bars represent the standard error.

The variation of Cu, Fe and Zn in the alga seems to reflect the variations of the above metals in the sediment and the variation of Cd in the plant followed by the variation of Cd dissolved in the seawater. Low concentrations of Cu and Fe in *G. verrucosa* reported in winter-spring when biomass was at a maximum [2], resulted in decrease of these metals per mass unit due to their dilution [e.g. 3]. Copper and Fe concentrations in the alga increased with tissue-age [e.g.4], whereas Cd ones decreased with plant-age [5]. The high levels of Fe, Cd and Zn in summer-fall can also be attributed to the fact that during these months plant photosynthesis and respiration are more intense thus enhancing algal metal uptake [6].

Cadmium of Pb concentrations in *G. verrucosa* in this study exceeded those in this or other species of the genus from other areas [7,8] and Fe and Cu levels were higher than those in the species in this area from previous study [9].

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TIME DEPENDENT PHASE ASSOCIATIONS OF IRON AND OTHER TRACE ELEMENTS ELUCIDATED BY ^{234}Th/^{238}U INVENTORIES IN TROPICAL COASTAL WATERS

XA9952043

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The in situ oxidation of iron plays an important role in the scavenging and subsequent particulate-phase transport and removal of other trace elements from coastal waters. Thermodynamically, the chemistry of iron in seawater is relatively well understood, conditions heavily favouring the formation of Fe(III) oxyhydroxides. However, a range of time dependent processes may induce significant departures from the anticipated equilibrium conditions, or severely retard the approach to equilibrium. Light has been shown to reduce and solubilise iron under acidic laboratory controlled conditions [1], suggesting that ferric oxyhydroxides can, in principle, be photo-reduced in seawater. However, the tendency is for photo-produced Fe(II) to remain at the particle surface forming a coating of relatively soluble amorphous iron oxides which limits major increases in solution phase iron [2]. Another complicating factor is the apparent ability of light to influence the size distribution of iron oxides, demonstrated in both laboratory and field experiments [2].

An understanding of time dependent particle formation and scavenging processes has been developed through observations of disequilibrium in the naturally occurring isotope pair ^{238}U and ^{234}Th. ^{234}Th with a half-life of 24.1 days and high affinity to bind with seawater particles, provides an excellent tracer to study processes with temporal ranges from days to months.

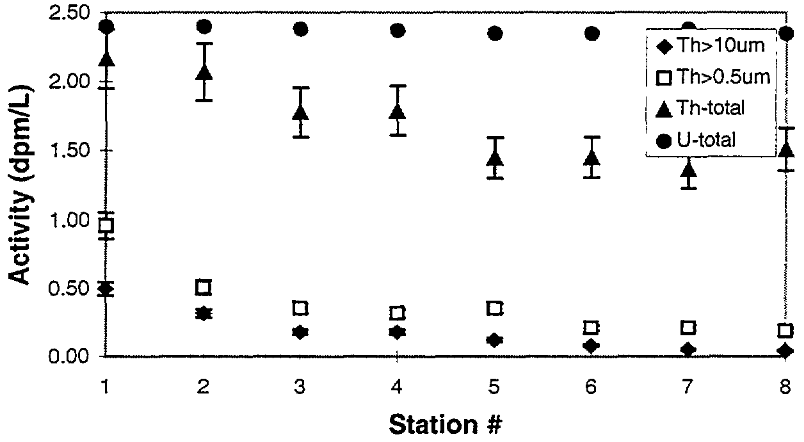

FIG 1. ^{238}U and ^{234}Th gamma activities in PNG coastal seawater.

In this study samples were collected in the Gulf of Papua region of PNG, on board the research vessel Franklin as apart of a multidisciplinary study of factors influencing the fate of terrestrial material entering the tropical coastal ocean. Samples for ^{234}Th were collected using a in situ large volume pump device (Challenger Oceanic) passing seawater (1000-2000 litres) through a series of cartridge filters in polycarbonate housings. The cartridges and analytical techniques are detailed elsewhere [3]. Trace metals samples were collected from an inflatable dinghy using teflon-lined 5 litre Niskin GoFlo samplers (General Oceanics) suspended by a polypropylene rope and polyethylene encased lead weight. Duplicate samples were immediately returned to the research vessel for filtration and extraction in a Class 3.5 containerised Clean Laboratory using a C-18 Sep-Pak immobilised 8-hydroxyquinoline technique and ICP-MS detection [3]. Final iron determinations were performed by Zeeman GFAAS.

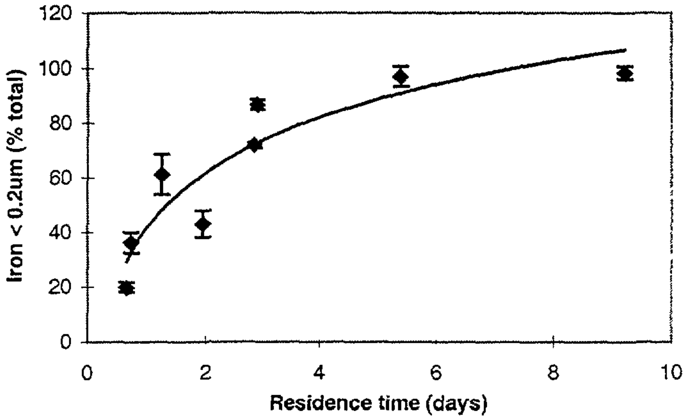

FIG 2. Proportion of total iron on particles less than 0.2μm

In the Gulf of Papua residence times of particles, deduced by 234-thorium/238-uranium inventories (Fig. 1) varied from less than 1 to more than 20 days. The particle size distribution of iron (Fig. 2) was observed to vary according to residence time in surface waters, with increased illumination retarding particle formation, favouring the persistence of a more reactive fine fraction (<0.2μm). Concentrations of several dissolved trace elements were observed to increase with increasing residence times of particles (Fig. 3), allowing for greater illumination of incident particles, persistence of fine particles with high surface area for release/uptake of metals, saturation of available sorption sites and retardation of scavenging, resulting in higher incident metals concentrations as the rate of supply exceeds the rate of removal.

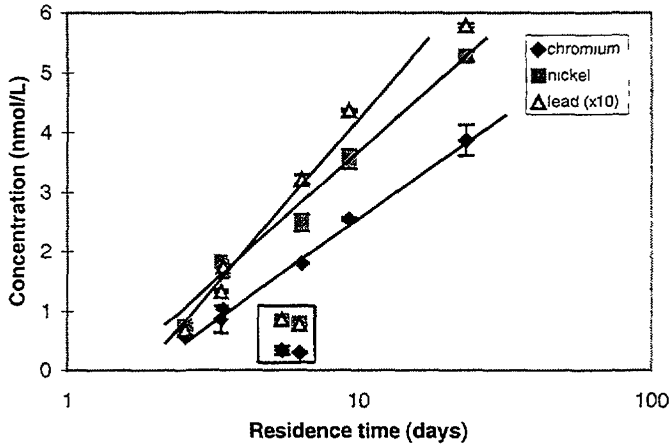

FIG 3. Dissolved trace metal concentrations versus residence times.

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IMPACT OF A COAL FIRED POWER PLANT ON ^{226}Ra ACTIVITY LEVEL IN SEA WATER

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The paper deals with radioactivity contamination originating from a coal fired power plant which, due to its location, may present a remarkable environmental problem. The plant is situated in a bay of the Adriatic close to the densely populated area with highly developed touristic activity. Its operation may cause significant damage to rich marine ecosystem characteristic for this part of the Croatian Adriatic as well as endanger urban and touristic developmental prospects of the area. Investigations of coal used in regular plant operation and of solid incombustible ash and slag showed increased natural radioactivity levels which may cause general environmental contamination of the bay as well as contamination of the marine environment of this part of the Croatian Adriatic [1].

Increase in radioactivity related to the plant and associated environmental risk should be determined in order to meet the regulatory or environmental protection requirements of the region which may involve introduction of a suitable disposal system or a new technology.

The coal with higher radioactivity level that has been prevailingly used over the past few years resulted with more active ash and slag. Subsequent to regular operation of the power plant ash and slag (^{226}Ra mean specific activity was 1490 ± 70 Bqkg^{-1}) were continuously dumped into a basin-like closed area and surplus water overflows directly into the sea.

Determination of radioactive contamination required analyses of four different types of samples: basin water, sea water at the site of overflow and sea water collected at two sites at some distance from the deposit basin. ^{226}Ra was determined by alpha spectrometric measurements using silicon charged particle detector. The counting time for each measurement was 60.000 sec or longer.

Figure 1 shows ^{226}Ra specific activity in waste-deposit basin water. Different ^{226}Ra specific activities correspond to different radioactivity levels determined in the coal depending on the kind of coal and different mining locations [1].

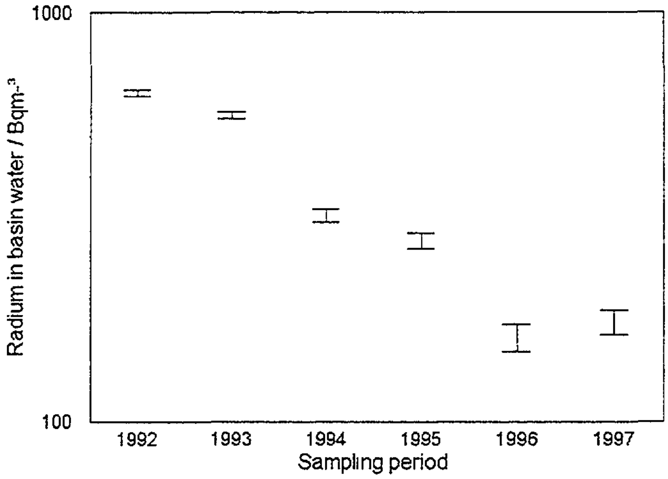

FIG. 1. ^{226}Ra specific activity in waste-deposit basin water.

Figure 2 shows correlations obtained for ^{226}Ra specific activity in the samples of sea water and basin water, and basin water and water at the point of overflow from the basin.

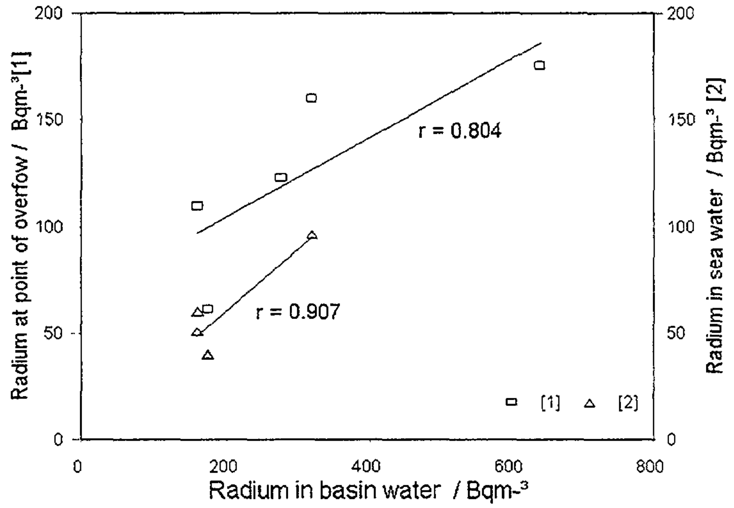

FIG.2. ^{226}Ra specific activity in sea water and water at the point of overflow in correlation with basin water.

Mean ^{226}Ra concentration determined in the samples of bay sea water was 51.3±29.2 Bqm^{-3} which is an order of magnitude higher than ^{226}Ra concentration in the Mediterranean Sea (3.7 Bqm^{-3}), as well as in the open Adriatic sea far from the plant deposit site [2].

All described investigations and measurements were carried out at the Institute for Medical Research and Occupational Health, Radiation Protection Unit, Zagreb. The data obtained in the study can serve as a valuable data base for future estimations of the impact of radioactive pollution to the marine environment and developmental prospects of the region.

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ENVIRONMENTAL IMPACT OF THE MINERO-METALLURGIC INDUSTRY ON THE MARINE ECOSYSTEM IN MOA, CUBA

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One of the biggest nickel mineral deposits of the world is located in Moa; therefore two plants are istalled for the extraction of this metal in the region, and another is in its construction phase. During the chnological processes, residuals that contain great quantity of metallic elements, and high acidity level are ischarged into the environment. The objectives of this research were to establish the levels of pollution of leven metals, Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn in the superficial bottom sediments, sea water d organisms of the marine aquatorium (green and white sea urchins, blue crabs, oysters and mangrove aves). The dynamics of pollution in superficial sediments was also determined in the course of a 9-year udy. As complementary analyses, pH and salinity were determined for the supradjacent water to the marine ottom, as well as the content of organic carbon, and granulometry of the sediment.

A network of 29 stations was established (GPS), covering the area of the reef lagoon between the S rea of the W end of Cayo Moa Grande until the NE of the mouth of Arroyo Semillero, with an extension of round 80 km^2. The samples of bottom sediment were taken by means of a mini-dredge, being stored in lastic bags of 2 kg. Then they dried off by liofilization, and the bioavailable heavy metal fraction was etermined (HCI 0,5N) using a plasm spectrometer (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn). The ioindicators studied were: *Tripneustes ventricosus, Lytechinus variegatus, Isognomon alatus, Rhizophora angle*, using atomic absorption spectrometry and cold vapor for Hg. Some sediment samples were analyzed sing an X-ray fluorescence spectrometer dispersive energy (FRXED) with the following characteristics: ources of excitement of Cd-109, A=14.1 mCi and Fe-55, A=18.9 mCi, with a Si(Li) detector; of with a 7 μm indow, 120 cm^3 of sensitive volume and an energy resolution of 197 eV. The APTEC system was used for ata acquisition.

The high value of the concentration baseline of the bioavailable fraction in sediments is a factor ausing great concern, because their chemical state allows them to pass with relative easiness through the ophic chain up to man (Table I). In Cayo Moa's Bay, there exist hydrological and environmental impact onditions that favor the accumulation of pollutants in this system (Martínez-Canals and García, 1977). When omparing the metallic contents with near areas, but with other characteristics such as the Bajo del hinchorro, it was established that they were 14 times richer in Co, 28 times in Cr, 10 times in Cu, 4 times in e, 27 times in Mn, 9 times in Ni and 16 times in Zn (Martínez-Canals et. al., 1993). The metallic oncentration gradually diminishes as sediments are more to the E of the industrial zone, away from Río Moa.

The pollution dynamics for heavy metals in superficial sediments after 9 years showed an nprovement in environmental quality (Martínez-Canals et. al., 1993; Martínez-Canals and García, 1997). he indexes of calculated micropollution (Papakostidis et. al., 1975) are in general smaller than those stablished in 1988-89 for the same stations, although the mean values are very similar. However, in 3 of the reas sampled in 1996 and 1997, indexes have increased several times in relation to 1989. This phenomenon explained because these stations are inside the area of influence of Río Moa (determined by LANDSAT atellite image of January 31, 1994), and the heavy metal content in superficial sediments increases in the ourse of the time.

When applying the agglomerate hierarchical method to the concentration values of the different areas, ray-Curtis index, 4 groups were obtained (in upward order of pollution level):

Interior area of coral reefs (N of Cayo Moa Grande and of Bajo del Chinchorro), and E coast of Moa City (clean area).
Sectors near the mouths of Moa and Yagrumaje rivers, Punta Gorda stream Cayo Guam.

- Entrance channel to the harbour, as well as its adjacent areas.
- Cayo Moa's Bay (most polluted sector with an average concentration 10 times higher than group 1).

With the employment of FRXED, we determined the concentration of 21 elements (Al, As, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Si, Sr, Ti, V, Y, Zn and Zr) in 12 samples of sediments, making the correction by absorption (carried out by B.Sc. Marlene Gómez). The results, compared with those carried out by EAA, didn't present statistically significant differences, F proof, from those obtained by atomic absorption spectrometry, with the exception of Cu (Table). The use of this technique is very usefull because it isn't neccessary the destruction of the samples, rapid analyses, good sensibility and precision in the study of samples for the evaluation of environment impact. Were define the proccedings for the preparation of the sediments, methods for the analyses of the spectrums and the correction of the matrix.

TABLE I. RESULTS

SEDIMENTS ($\mu g.g^{-1}$)

Atomic absorption and induced plasma spectrometry

1996-1997

Al	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
5316.3	3.5	70.4	654.8	35.8	4271.2	0.10	1518.9	807.9	61.1	228.3

1988-1989

Co	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
155.2	1874.5	57	29700	10528.3	1360.5	168.1

X-ray fluorescence

ELEMENT	MEAN	RANGE	ELEMENT	MEAN	RANGE
Al (%)	**1,7**	**0,4-3,7**	**Ni**	**1193,2**	**135,0-4400,0**
As	**17,0**	**2,8-36,0**	**Pb**	**46,7**	**10,6-159,0**
Br	**215,3**	**34,3-1360,0**	S(%)	**0,3**	**0,1-0,9**
Ca(%)	**19,3**	**0,5-32,0**	Si(%)	**2,7**	**0,3-7,9**
Cl(%)	**5,9**	**0,6-13,6**	**Sr**	**2402,8**	**36,8-4600,0**
Cr	**2747,4**	**287,0-8620,0**	**Ti**	**938,0**	**0,3-3911,0**
Cu	**269,5**	**67,7-738,0**	**V**	**145,4**	**21,5-385,0**
Fe (%)	**14,9**	**1,1-44,5**	**Y**	**45,4**	**1,0-452,0**
K	**1288,0**	**11,0-3760,0**	**Zn**	**217,1**	**47,3-565,0**
Mn	**2122,33**	**68,6-13000,0**	**Zr**	**41,1**	**4,4-91,0**

SEA WATER ($mg.L^{-1}$)

Atomic adsorption spectrometry

Al	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
0.63	0.03	0.26	0.05	0.04	0.10	0.02	0.28	0.05	0.70	0.02

MARINE BIOTA ($\mu g.g^{-1}$)

Atomic adsorption spectrometry and cold vapour (Hg)

Estac.	Organism	Part	Al	Co	Cr	Cu	Fe	Mn	Ni	Zn
10	Oysters	Soft tissue	764	3.7	54	7.1	1946	136	38.2	1823
	Mangrove	Leaves	97.3	0.4	55.5	4.6	312	531	7.0	4.4
13	Urchins W.	Skeleton	277	24	129	31	49.8	615	58.5	11.3
14	Mangrove	Leaves	63.8	0.3	2.3	1.9	159	425	4.4	6.4
15	Oysters	Soft tissue	2050	0.99	73	0.5	243	179	45.3	2525
19	Urchins W.	Skeleton	251.6	23.0	193.3	56.7	40.3	66.7	35.0	441.5
		Gonades	110.2	10.7	45.5	23.3	81.9	252	33.6	11.3
20	Crabs	Soft tissue	270	20	42	111	45.2	12.7	44.3	11.3
23	Urchins G.	Skeleton	270	24	97	0.5	67.2	147	35.3	1102
	Urchins W.	Skeleton	143.3	36.3	109.7	41	52.5	615.7	80.7	1161
28	Urchins G.	Skeleton	32.9	0.2	0.3	0.3	44.1	59.7	1.2	8.8
	Urchins W.	Skeleton	44.1	0.1	0.5	0.1	55.5	288	0.68	7.2
33	Oysters	Soft tissue	747	3.4	46	7.7	1369	122	36.8	1865
	Mangrove	Leaves	50.4	0.2	2.5	1.3	144	283	2.8	1.4

In sea water the concentrations of Cd, Co, Cu, Hg and Pb showed smaller values than the detection imits of the method employed, Table 1. The Río Moa's mouth presented the maximum concentrations of Al, Cr, Fe, Mn and Zn, possibly due to the dissolved elements coming from the waste lines and/or residual waters of the nickel-producing enterprises, to the low pH (6.9) and salinity (30 %) values. These factors cause the dissolution and/or resolution of metallic elements and the decrease of floculation, precipitation and sedimentation processes of the suspended matter. When comparing the contents with those in sediments in he same areas, it was observed that where the highest values were obtained in bottom sediments they corresponded to the lowest values in water. This is due to the metallic accumulation in the solid matrix due to he precipitation of these elements in the mentioned areas, such as Cr and Mn.

Oysters, *Isognomon alatus*, presented the highest metallic contents, especially those collected at Las Camariocas, micropollution index=5.65, which presented the maximum values of Al, Fe and Zn (Table). The white sea urchin, *Tripneustes ventricosus*, (collected at the entrance channel of the port), presented the maximum values of Cr, Cu and Mn in its skeleton. Mangrove leaves, *Rhizophora mangle*, showed an apparent nverse relationship between the health status of the mangrove swamp and the heavy metal content.

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DISTRIBUTION OF ^{129}I: EVIDENCE FOR WORLD-WIDE INFLUENCE OF NUCLEAR FUEL REPROCESSING

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Iodine-129 is one of the radioisotopes which have seen significant increases in the environment since the beginning of the nuclear age. Other prominent representatives of this group include tritium, ^{14}C and ^{36}Cl. Most members of this group have gone through a cycle of initial release (associated mainly with atmospheric bomb tests during the late fifties and early sixties) and subsequent decay (e.g. T) or dispersion (e.g. ^{14}C and ^{36}Cl) so that their concentrations are again close to pre-anthropogenic levels. ^{129}I has, however, remained at significantly elevated levels even after the stop of nuclear weapon tests. The main reasons for this behavior are a combination of long half-life (15.7 Ma), relatively low natural [1] and significant contributions from anthropogenic sources other than nuclear weapons tests. While during the early development of nuclear power stations ^{129}I was frequently released during routine operations, the current high level of this isotope is most likely related to the continuous release from the reprocessing of nuclear fuel [2, 3]

Given the specific behavior of ^{129}I, it is not surprising that this isotopic system has been frequently mentioned as a potential tracer in young aquifers, of ocean circulation [4, 5, 6] and as tracer for the origin of organic material in marine sediments [7]. The further application of this isotopic system depends critically on a sound understanding of the distribution and pathways of anthropogenic ^{129}I. A number of studies have looked at the distribution of ^{129}I at a specific site [3, 4] or associated with a specific source [8, 2]. We present here a compilation of ^{129}I concentrations in fresh waters on a world-wide basis. Typical sample size for the determination of ^{129}I concentrations and ^{129}I/I ratios surface water samples was between 500 mL and 1L. Iodine concentrations were measured either using ICP-MS or ion chromatography. For the determination of ^{129}I/I ratios, carrier iodine was added to the samples in order to collect at least 1 mg of AgI. Ratios reported here were measured using the AMS system of PRIME Lab (Purdue University).

The majority of the data were collected in North America, but we have now also data from many other parts of the world, including results from the southern hemisphere. The lowest concentrations of ^{129}I were found in the Arctic, western coastal areas of North America and in New Zealand. Concentrations (given here in (^{129}I atoms)/mL) in these areas are typically below 10 atoms/mL, with the lowest concentration found so far in Lake Wairapapa, NZ (0.34 atoms/mL). Levels determined in other parts of New Zealand, in Australia, Costa Rica and Washington State are between 1 and 10 atoms/mL . In contrast to these relatively low levels, concentrations found in the eastern United States and Canada as well as in Europe are considerably higher, typically by factors between 10 and 100. The highest values were measured near reprocessing plants, as for example near West Valley in Western New York State where concentrations reach values above 10^5 atoms/mL [2].

The distribution of ^{129}I clearly indicates that this radioisotope is still significantly above pre-anthropogenic concentrations on a world-wide basis. Even the lowest values found so far are still two orders of magnitude above the calculated level for pre-anthropogenic ^{129}I in water. An estimate of the total amount of bomb-produced ^{129}I is too low to explain the observed levels of ^{129}I in both hemispheres. In the northern hemisphere, the pattern of distribution is strongly dominated by releases from reprocessing plants while active nuclear power plants do not seem to have a major impact on the distribution of ^{129}I. The observation that elevated levels of ^{129}I are also found in the southern hemisphere even in areas without any history of nuclear activities (e.g. New Zealand) indicates that the distribution of ^{129}I releases from reprocessing plants has a strong and persistent influence on the world-wide concentrations of this radioisotope.

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IAEA-SM-354/177P

GEOGRAPHIC AND VERTICAL DISTRIBUTION OF GLOBAL FALLOUT AMERICIUM 241, PLUTONIUM ISOTOPES AND CESIUM 137 IN LAKE SEDIMENTS

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239-240 and 238 plutonium, 241 americium and 137 cesium were introduced in global environment systems from a series of nuclear weapons tests that started about 45 years ago [1]. For cesium the accident of Chernobyl in 1986 increased the fallout.

European terrestrial and aquatic sites show a wide range of environmental concentrations and flux of the radionucides fallout. As contributions from existing nuclear industry are still very limited, the mentioned variations in plutonium and americium levels are obviously related to large scale and long term forcing process. Such processes are poorly understood especially when considering the diversity of European freshwater systems [2].

In this study, we present results concerning the activity concentrations of ^{241}Am, $^{239-240}$Pu, ^{238}Pu and ^{137}Cs in lake sediments. Bulk cores for radionuclide inventories and high resolution cores for depth distribution are analysed.

The plutonium and americium analysis were made by alpha spectrometry [3-4] and cesium analysis by gamma spectrometry [5]. But for americium and plutonium a radiochemical separation and extraction are necessary before the measurement.

An useful method is applied with a preconcentration step by calcination, acid nitric leaching and ferric coprecipitation. The separation is made with an anionic exchange column in acid nitric medium. Americium, iron, rare earth, radium, polonium, uranium passed through the column. Thorium is eluted with hydrochloric acid and plutonium with hydrochloric acid + ammonium iodide.

The americium fraction is also separated by a radiochemical process using an oxalate coprecipitation, a liquid-liquid extraction with HDEHP or DDCP, a double ion exchange column (cationic + anionic) and then an ion exchange column in acid - methanol medium.

Solutions are then electroplated on stainless steel disks.

With these results, we have compared the behaviour of plutonium, americium and cesium. Vertical profiles for these elements are shown and isotopic ratios (^{238}Pu/$^{239-240}$Pu, $^{239-240}$Pu/^{137}Cs, ^{241}Am/$^{239-240}$Pu) are calculated. The migration and mobility of the elements in the sediments and their activity concentrations according to different sites in the lake (catchement area, accumulation basin) are studied.

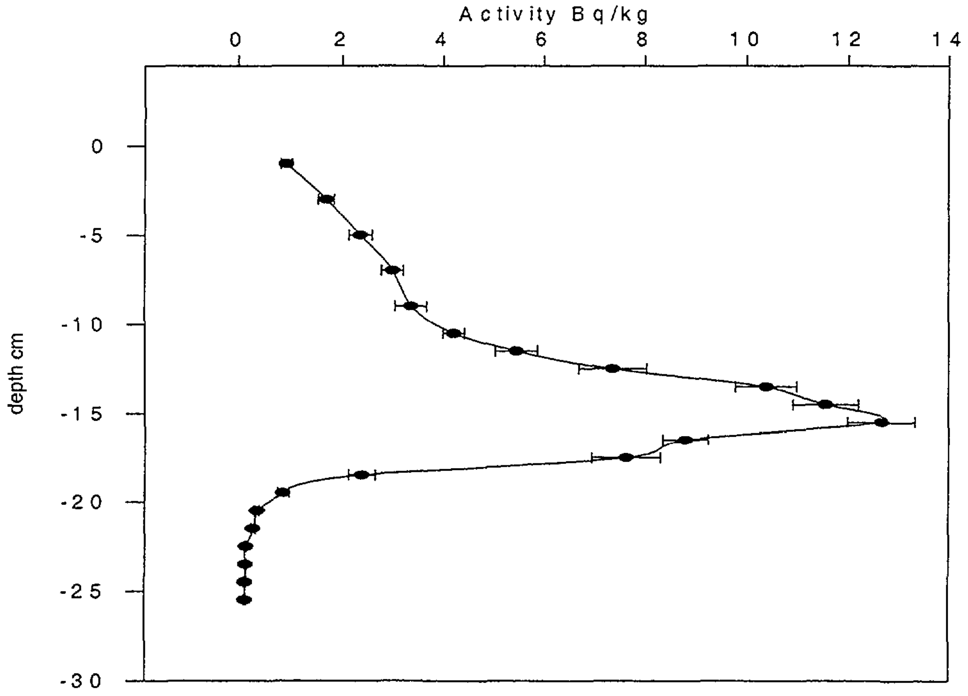

FIG. 1: Vertical profil of 239-240 Pu.

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IAEA-SM-354/178P

USING STABLE CARBON AND NITROGEN ISOTOPE RATIOS FOR UNDERSTANDING TROPHIC STRUCTURE IN THE SETO INLAND SEA, JAPAN

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Stable isotope ratios of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$) are very useful for analyzing trophic structures in the biosphere, because $\delta^{13}C$ and $\delta^{15}N$ are indices for food sources and trophic levels. We examined $\delta^{13}C$ and $\delta^{15}N$ in zooplankton and fish collected over the whole area of the Seto Inland Sea, Japan, in order to clarify trophic structure.

The zooplankton samples were collected by vertical towing with a plankton net (mesh opening of 100 µm) over the whole area of the Seto Inland Sea during the period 1993 - 1995. These net-plankton samples were separated into species by the pipette technique before storing at -20 ∞C. Suspended particle samples were collected during the period 1993 - 1994 in Osaka Bay. Fish samples were also collected by fishing nets in Osaka Bay in 1995. For the fish samples, we separated-out only muscle tissue, which was then stored at -20 ∞C. These samples were freeze-dried before isotopic analysis.

Samples were measured for $\delta^{13}C$ and $\delta^{15}N$ by an on-line analytical system joining a stable isotope analyzer (Finnigan Mat, Mat 252) with an elemental analyzer (Carlo Erba NA-1500), as described previously [1].

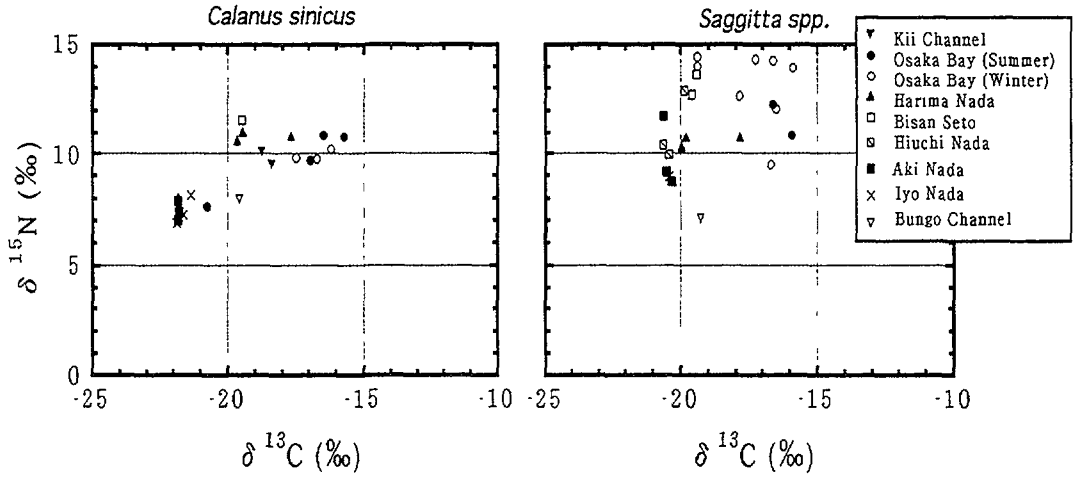

FIG.1 $\delta^{13}C$ and $\delta^{15}N$ of typical herbivorous (Calanus sinicus) and carnivorous (Saggitta spp.) zooplanktons in various areas of the Seto Inland Sea.

Fig. 1 shows the $\delta^{13}C$ and $\delta^{15}N$ for typical herbivorous (*Calanus sinicus*) and carnivorous (*Saggitta spp.*) zooplankton in various areas of the Seto Inland Sea. The $\delta^{13}C$ of *C. sinicus* collected in Osaka Bay were observed to have the highest values (more than -16â), and those collected in the Aki Nada and Iyo Nada areas to have the lowest values (-22â). In general, the $\delta^{13}C$ of *C. sinicus* tended to be higher in the eastern part of the Seto Inland Sea. The $\delta^{15}N$ of *C. sinicus* collected in the eastern parts of the Seto Inland Sea were also higher (nearly 10â) than those collected in the western parts (nearly 7.5â).

The δ^{13}C of *C. sinicus* depend on food. In the eastern part of the Seto Inland Sea, which is an eutrophic area, the high δ^{13}C of these (herbivorous) zooplankton were strongly influenced by the ratios of the food phytoplankton, which, in turn, were responsible for the high local primary productivity [2]. Generally, the δ^{15}N is known to be an index of trophic levels. However, it was found that the δ^{15}N of *C. sinicus* differed according to where they were collected in the Seto Inland Sea. It was considered that the δ^{15}N values of *C. sinicus* were primarily dependent on the δ^{15}N of their food. Therefore, the δ^{15}N of *C. sinicus* varied throughout the sea's area according to the type of prey phytoplanktons, which, in turn, varied in type according to the differences in nutrient sources. Therefore, in the Seto Inland Sea, we can make trophic level estimations for such higher trophic level organisms by making use of stable isotope ratios.

The δ^{15}N of *Saggitta spp.* tended to be higher than for *C. sinicus*. Moreover, greater or lesser differences between the ratios of *Saggitta spp.* and *C.sinicus* were observed according to season and the different sea areas in which they were collected. These results showed that the lower level trophic structures in the Seto Inland Sea differed according to the location of the sampling site and season in which the plankton were collected.

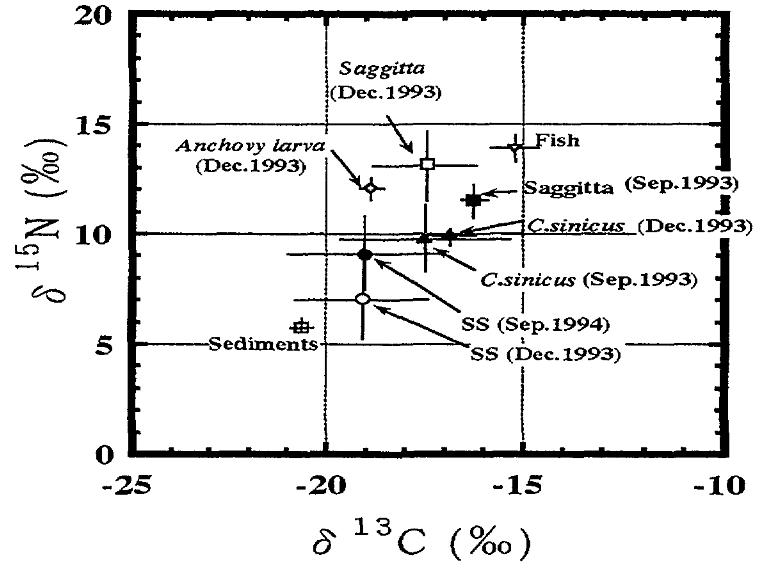

FIG. 2. Relationships between δ^{13}C and δ^{15}N of particulate matter (SS), zooplankton, fish, fish larva and sediments in both summer and winter in Osaka Bay.

Fig. 2 shows the relationships between δ^{13}C and δ^{15}N of particulate matter (SS) , zooplankton, fish, fish larva and sediments in both summer and winter in Osaka Bay. In this figure, the length of the bar indicates one standard deviation of the data set. In summer, δ^{13}C and δ^{15}N were not significantly different between particulate matter and *C. sinicus*, and between *C. sinicus* and *Saggitta spp.* On the other hand, in winter, the δ^{15}N were significantly different. These data suggest that in summer, a very complex feeding pattern exists throughout the food web of these microorganisms, while a simple (monocultural) grazing food web applies in winter.

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RESULTS AND ANALYSIS OF THE ARMARA SEA WATER INTERCOMPARISON FOR ^{137}Cs, ^{238}Pu AND ^{239,240}Pu

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With the initiation of the EC-supported Arctic Marine Radioecology (ARMARA) project in late-1995, the need to ensure comparability of radionuclide measurement in sea water between the participating laboratories became apparent, as extensive data sets obtained in the course of separate expeditions, sometimes using different preconcentration and radiochemical techniques, were combined for modelling purposes.

Accordingly, the collaboration decided to undertake the analysis of a large-volume sea water sample in order to check the internal consistency of its sea water data. Sample collection and distribution was carried out by the Bundesamt für Seeschiffahrt und Hydrographie (Hamburg). Each participant laboratory received 600 litres of North Sea surface sea water collected from aboard the *R.V. Gauss* on the 3rd of November 1996 at 55° 23.0'N, 04° 30.0'E. It was assumed that the well-mixed nature of these waters during this season of the year, together with the special precautions taken during the filling of the individual containers ensured, in so far as was practicable, the homogeneity of the sample set.

The radionuclides measured included ^{90}Sr, ^{99}Tc, ^{137}Cs, ^{238}Pu, ^{239,240}Pu and ^{241}Am, though not all of the participants committed themselves to analysing each one of these nuclides. Here, the results for ^{137}Cs, ^{238}Pu and ^{239,240}Pu are presented (Fig. 1), together with a statistical analysis of the data and some comments on the overall result.

The means submitted by the participants were tested for outliers using the Dixon test. Median (and mean) values were then calculated for all of the results passing the test. These values were considered to be the most reliable estimates of the unknown true values. Confidence intervals were taken from a non-parametric sample population [1] and represent a two-sided interval at a significance level of 0.05.

Of the fourteen values reported for ^{137}Cs, none was rejected as an outlier. The range of accepted laboratory means is 10.4 – 15.0 Bq m^{-3}; the median is 12.75 Bq m^{-3}, with a confidence interval of 11.9 – 14.1 Bq m^{-3}. In the case of ^{239,240}Pu, eleven laboratories reported their results. All passed the outliers test. The range of laboratory means is 14.0 – 23.0 mBq m^{-3}, and the median is 16.7 mBq m^{-3}, with a confidence interval of 14.0 – 19.8 mBq m^{-3}. For ^{238}Pu, seven results were reported, all passing the outlier test. The range of laboratory means is 1.5 – 3.0 mBq m^{-3}, the median is 2.2 mBq m^{-3} with a confidence interval of 1.5 – 3.0 mBq m^{-3}. For all three data-sets, the mean of the reported values was very similar to the median, indicating a near-symmetrical probability distribution of the parent population.

Code	^{137}Cs (Bq m ^{3})
K	10 4 ± 1 0
E	11 8 ± 0 5
A	11 9 ± 0 5
G	11 9 ± 0 6
B	12 1 ± 0 9
L	12 4 ± 0 3
I	12 7 ± 0 8
M	12 8 ± 1 1
J	13 0 ± 0 4
D	13 4 ± 0 5
N	14 ± 2
C	14 1 ± 1 4
H	14 7 ± 0 7
F	15 0 ± 0 6

Code	$^{239\,240}$Pu (mBq m ^{3})
B	14 0 ± 1 2
I	14 0 ± 1 4
E	15 3 ± 1 0
M	15 3 ± 2 8
F	16 5 ± 1 4
K	16 7 ± 1 1
D	17 1 ± 1 0
A	17 2 ± 1 3
G	19 1 ± 1 0
J	19 8 ± 0 8
N	23 ± 5

Code	^{238}Pu (mBq m ^{3})
I	1 5 ± 0 3
K	1 5 ± 0 4
A	2 1 ± 0 4
B	2 2 ± 0 4
E	2 3 ± 0 2
G	2 8 ± 0 4
J	3 0 ± 0 3

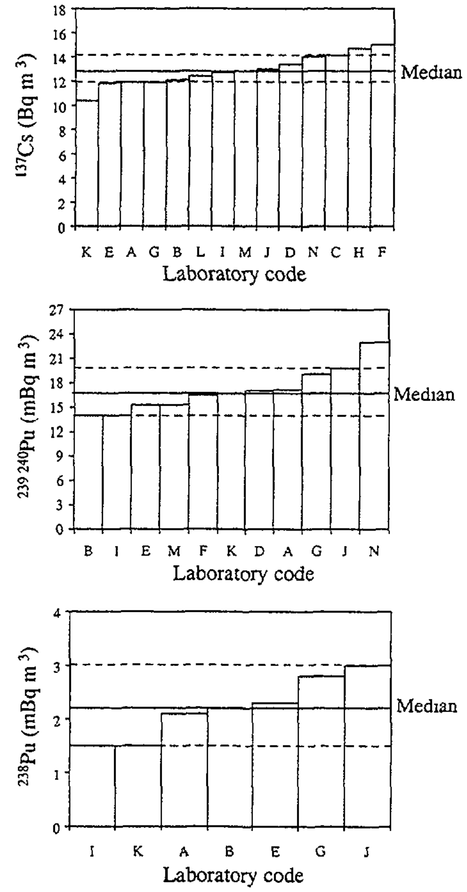

FIG. 1. Reported ^{137}Cs, ^{239,240}Pu and ^{238}Pu concentrations (± 1σ). The dashed lines in the figures indicate the 95% confidence intervals of the respective medians

The agreement between the results submitted by the participants in this internal exercise is considered to be satisfactory, given the low activity concentrations involved. We are, thus, confident that data being reported by collaborating laboratories within the framework of the ARMARA project are consistent and that an appropriate level of intra-laboratory quality control is in place. An indication of the overall quality of the data can be obtained from the widths of the confidence intervals around the respective medians [2]. Comparison of our values with those obtained in IAEA-organised intercomparison runs shows our results to be comparable with those generally considered to reflect good quality data.

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XA9952050

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DISTRIBUTION AND TRANSFER OF DISSOLVED TRACE METALS IN THE NORTH AEGEAN SEA

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Sampling for trace metal analysis in the North Aegean Sea took place from 13-25 May 1997 with the R/V Aegaeo. Samples were collected from 12 Go-flo bottles attached to the rosette-CTD system and were filtered through 0.45 μm membrane filters, on-board, under a nitrogen atmosphere. Precautions were taken during handling of samples to minimise contamination. The samples were acidified and carried back to the clean laboratory for further analysis. A preconcentration step using the chelex-100 resin followed. Trace metals were determined on a Perkin-Elmer AAS equipped with a HGA-700. The recovery of the resin and the accuracy of the measurements were tested using a spiked seawater sample and NASS-4 reference seawater. Copper and nickel have been determined in three stations IR-43 (LAT 40°04′E, LONG 25°33′N) IR-16 (LAT 40°39′E, LONG 25°36′N) and IR-11 (LAT 40°39′E, LONG 24°24′N) and the results were related to the salinity-temperature data. The aim of this work is to study the distribution of trace elements in the North Aegean Sea and to identify possible trace metal enriched water masses.

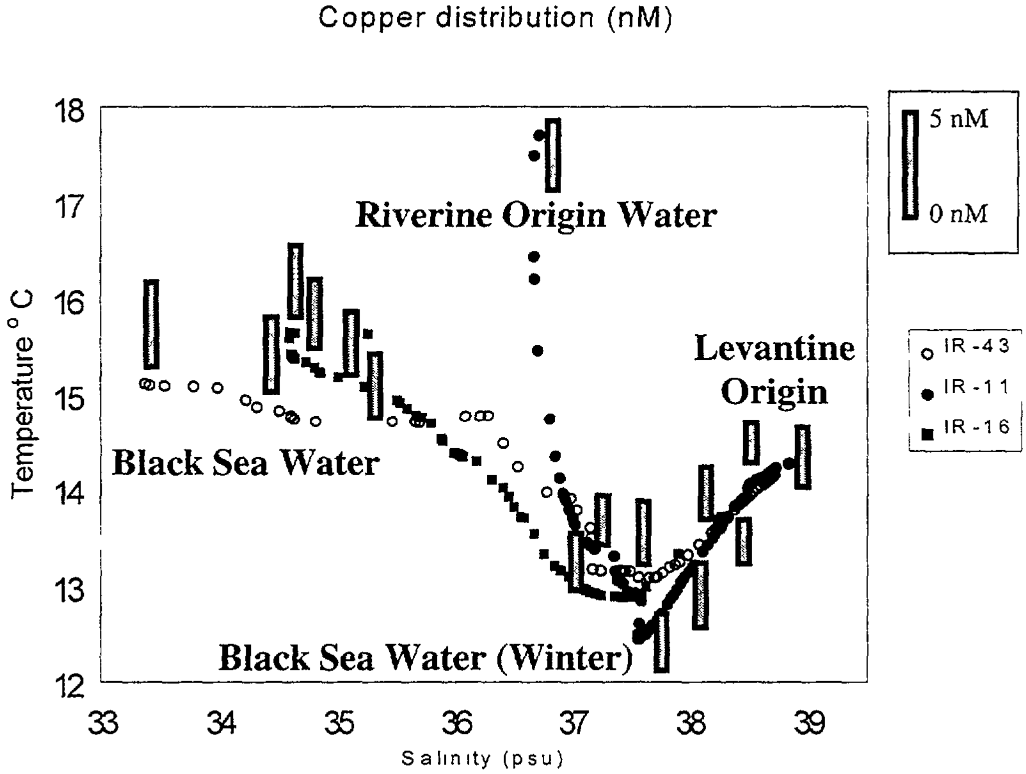

FIG. 1. T-S diagrams from three stations in the North Aegean Sea and copper concentrations in May 1997.

The North Aegean Sea is the region where the Mediterranean receives waters from the Black Sea through the Dardanelle Straits. The low salinity waters from the Black Sea enter the Aegean as a surface current, forming a strong frontal structure in their boundaries with the lightly saline and warm Mediterranean waters. In May 1997 CTD data were collected along with samples for dissolved trace metal analysis. At that time, the current Black Sea inflow was limited to the top 25 m of the water column, while a mixture of Black Sea water that had entered the Aegean during the previous winter and salty Mediterranean water occupied the layer between 30 and 100 m. The depths between 100 and 300 m were occupied by highly saline (~39.1‰) water of levantine origin and the deeper layers by locally formed waters.

In Figures 1 and 2, temperature-salinity diagrams are presented for the three stations along with the values of copper (in nM) and nickel (in nM) respectively.

Black Sea water seems to be associated with higher values of both copper (~4 nM) and nickel (~7.5 nM). Riverine water (surface water at station IR-11) has relatively enhanced values (3.72 and 4.18 nM, for copper and nickel, respectively. However, metal distribution was quite uniform in the other water masses (Black Sea winter water and Levantine origin water). Copper concentrations ranged between 2.21 and 3.72 nM and nickel between 3.47 and 4.15 nM. These values fall among the levels reported by other reserchers for the western Mediterranean [1]. Further analysis and correlation with other oceanographic data are under investigation.

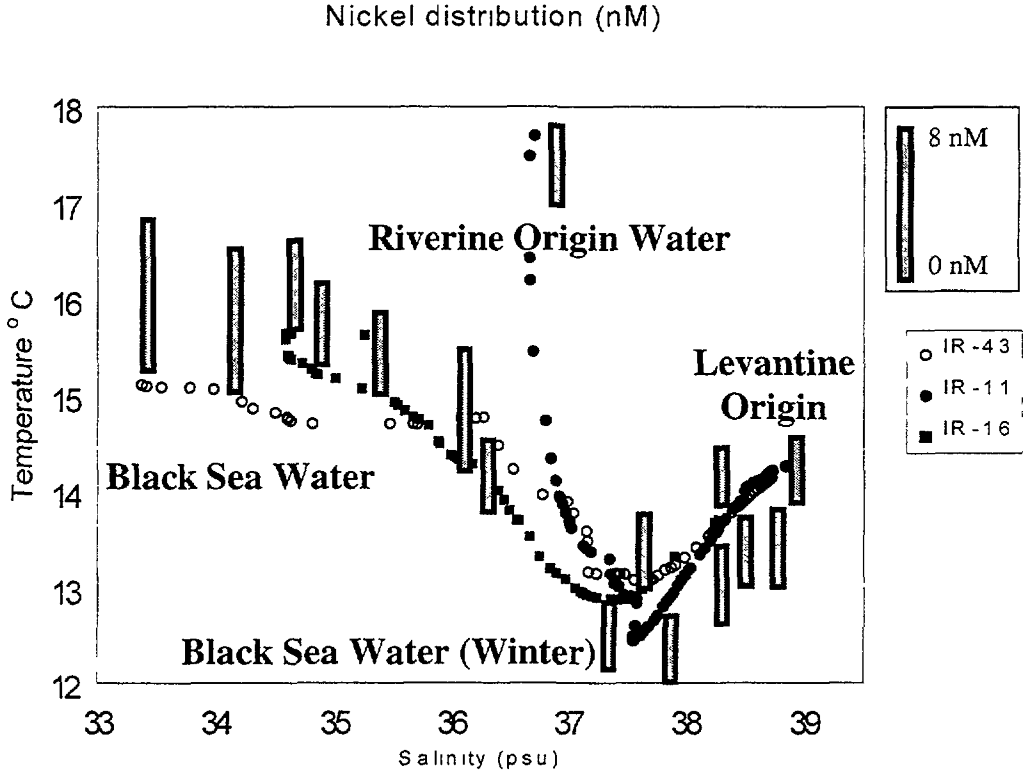

FIG. 2. T-S diagrams from three stations in the North Aegean Sea and nickel concentrations in May 1997.

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XA9952051

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COPRECIPITATE MECHANISM OF TRACE ELEMENTS IN COASTAL ENVIRONMENT FORMATION AND STRUCTURE OF PLURAL HYDROXIDE

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Trace metal is removed by scavenging processes in river, ocean, etc., especially coastal area. The scavenging reactions are occur with inorganic and organic colloidal matter. Their colloidal matters are so called carrier. Inorganic colloid is very important for scavenging reaction. The inorganic colloid is almost composed by some transition metal ions. But scavenging mechanism were not explained till now. The carriers compose not only single kind of metal ion but also many kinds of metal ions multi metal ions colloidal matter. For example Fe-Al-SiO_2 colloidal matter so called multi-dimensional component hydroxide matter. It seems that scavenging process in natural water systems are occurred with the multi-dimensional component hydroxide matter. The reaction and structure of multi-dimensional component hydroxide matter were studied. (I) Single component Coprecipitation processes of selenium with iron(III) hydroxide, aluminium(III) hydroxide and multiple component hydroxide of Al(III), Fe(III) and Si(IV) carriers respectively were investigated. Samples were prepared the various systems of carrier components by heterogeneous precipitation (The method was precipitated with adding acid and alkaline solution in carrier component solution at pH1. 5) and flash precipitation (The method was flash precipitated with adding carrier component solution at pHl.5 and then solution on pH adjusted 1.0~13.0). Distributions of particle size fractions in the precipitates were filtered with membrane filter (pore size: 3.0, 0.3 and 0.05~m, respectively). Metal ions of carrier and trace element in the samples were measured with Hitachi model 19~0 III Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES). (2) Double and multi component system distributions of the particulate size fractions were varied with variation of pH. The results are shown Fig. I such as mono, duality and tertiary system of Fe(III), Al(III) and Si(IV) sample solution systems by the flash precipitation method. In Fe-Al mixed system the colloid of Fe(III) ion by the flash precipitation was given small size panicle in the pH range from 4.0 to 6.0. But hydroxide aluminium(III) is dissolved in that pH range. In the case of the pH range from 8.0 to 12.0, the results suggest, that. Hydrolysis of Fe(III) component are caught Al(III) hydrolysis species and then precipitate. The precipitation matter is considered to form heterogeneous poly nuclear complex between Fe(III) and Al(III) ions. The precipitation matters are formed small colloidal state at the pH range of 4.0 to 6.0. Because of the ion radius and degree of dissociation has little difference. At the multi component carrier system, Si(I Vi and Se(IV) were precipitated for various panicle size precipitation matters. The results suggest Si(IV) is a product of heterogeneous poly nuclear complex which is good agreement with structure of aluminosilicate. (3) River water system River water samples were collected from the Aidu River system, Wakayama Prefecture, Japan in November of 1996. The water samples were filtered by membrane filter (0.3pm pore size) and then filtrates were separated by Sephadex G-15 gel filtration (molecular weight cut-off 1500). Separated samples were measured with Hitachi model Z-9000 Atomic Absorption Spectrometry (AAS) and Jasco V-520 UV/VIS Spectrophotometer. Results of the river water samples by gel filtration existed hydroxide carrier at the upper stream (Fig.2). Hydroxide carrier in the river was characterised by various factors, pH, water temperature, ionic strength, concentration and chemical species of hydroxide products, etc. It follows the carriers of hydroxide are shown to exist at heterogeneous poly nuclear complex in this river system. The scavenging process of materials in natural water with hydroxide is indicated by control I in g for trace elements at coastal environment.

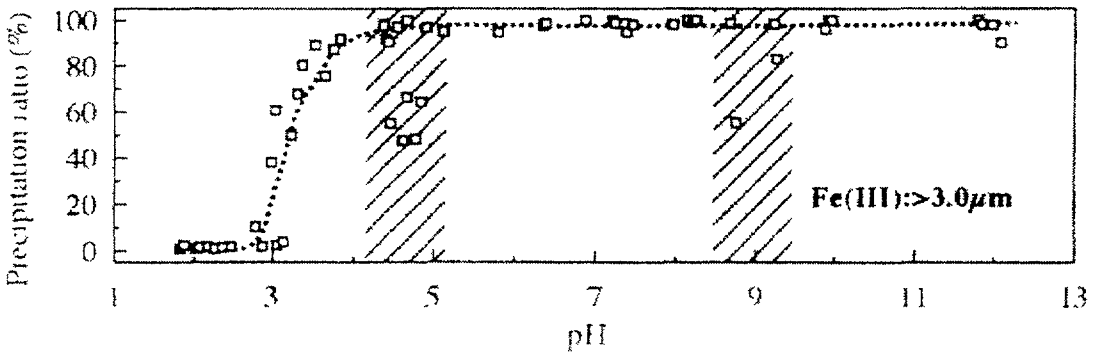

FIG. 1. Effect of pH on particle size distributions of iron and aluminium in Fe(III), Al(III), Si(IV) and Se(IV) mixed solution.

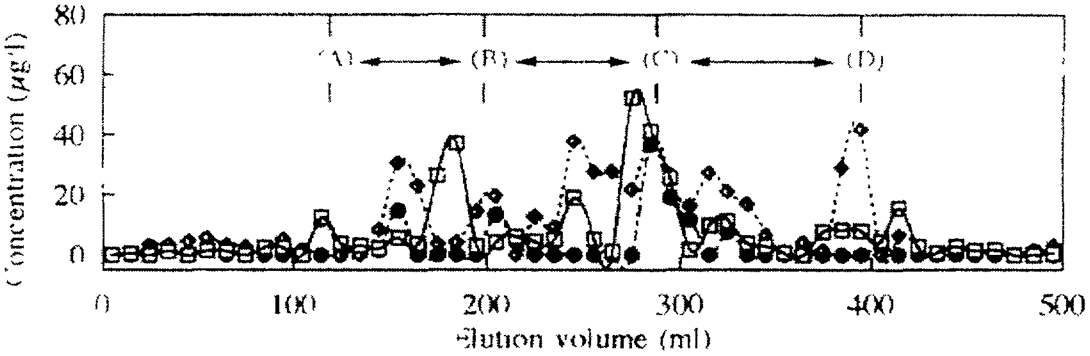

FIG. 2. Elution profiles of the water sample collected from the Aizu River after the gel filtratuion with Sephadex G-15

—□— Fe ---◆--- Al ---●--- SiO_2

Column	:3.6×50 ㎝	Eluent	:pH7.65, 0.5%-NaCl soln.
Bed dimension	:3.6×40 ㎝	Eluent speed	:3.97 ml/min

(A) : Molecular weight fraction (M.W.≧1500)
(A)~(B) : Molecular weight fraction
(B)~(C)(1500≧M.W.≧500)
(C)~(D) : Molecular weight fraction (500≧M.W.≧100)
: Molecular weight fraction (M.W.≦100)

IAEA-SM-354/185P

APPLICATIONS OF ARTIFICIAL RADIOTRACERS IN STUDIES OF SEDIMENT AND CONTAMINANT TRANSPORT IN THE COASTAL ZONE

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The role of radioisotope tracer techniques in support of coastal engineering has changed over the years. In the past tracers were one of the important sources of basic information in the investigation phase. Now, the primary tool in such investigations is the numerical or physical model and tracer techniques are used for model validation. Although the role of tracers has changed, their importance in model validation has grown with the ever-increasing reliance on model predictions for engineering and environmental decisions.

As the demands on the models grow, it is becoming increasingly important to understand the fundamental bases on which they are based. Indeed, the need for enhanced understanding of sediment and contaminant transport under extreme sea conditions and over extended scales of space and time is the major driving force behind the technology because only with radiotracer technology can actual observations be made on sediment movement over the long periods (up to one year). This is necessary if there is to be a reasonable prospect of capturing the impact of extreme storm events, etc. Such observations are essential for model validation.

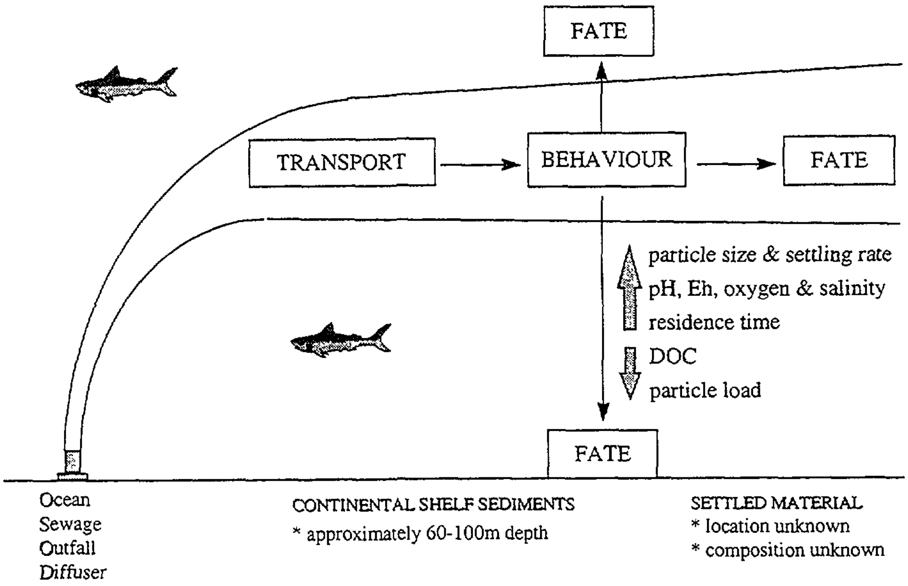

FIG. 1. Behaviour and fate of deepwater Outfall Sewage.

However, predicting sediment and contaminant transport in the coastal zone is difficult because of the complexity of hydrodynamics and water-particle interactions. It is also because wastes usually are not homogeneous, instead, they usually are composed of a variety of particles with different densities and are not uniformly diluted. A discharge frequently takes the form of the incident turbulence and is modified by ambient flows (such as coastal or estuarine currents), the presence of boundaries (such as the sea bed or surface), or density stratification, which may occur in estuaries and coastal waters. Further difficulties occur when municipal and industrial managers using multiple jets from multiport diffusers try to estimate mixing zone dilution.

Although some mathematical models are available for predicting hydrodynamics in the ocean, heir reliability sometimes, particularly when particles are to be introduced, is questionable because of the ack of fundamental knowledge about the mechanism of fluid-particle interactions and of particle urbulent dispersion itself. Some scale-model studies of specific cases were conducted in the laboratory. However, the laboratory studies cannot simulate all flow features. Thus, field studies using radioisotope racer technology are necessary to provide verification of computational models for sediment and ontaminant transport in the coastal zone.

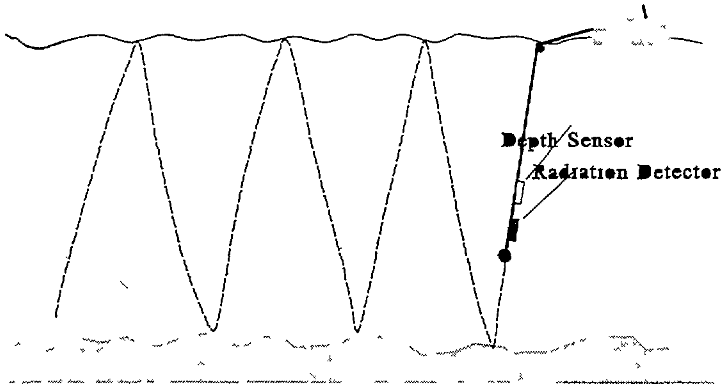

FIG. 2. In situ technique for sewage plume tracer study.

In this study performed in the Sydney coastal zone and adjacent continental shelf, a number of mportant questions associated with the fate of the contaminant transport from the ocean outfalls will be ddressed through a systematic work of radioisotope tracer measurements coupled with chemical and physical oceanographic measurements. The tracer study will provide unique data for the validation of omputational models developed in parallel by the research. Focus is given to dynamic processes relating o the fate and chemical behaviour of particles and associated trace element contaminants. Tracer xperiments are used to elucidate in situ kinetics of flocculation and particle formation processes [1] and how these relate to dispersion and transport [2]; (de)soprtion of particle associated chemicals; speciation hanges along the plume track; sedimentation [1]; sediment transport along the continental shelf and the nfluence of diagenisis processes [3].

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XA9952053

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RADIOACTIVITY OF SOME ALPHA, BETA AND GAMMA EMITTING RADIONUCLIDES IN SURFACE MARINE SEDIMENTS OF DIFFERENT BAYS IN ALGERIA

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Samples of surface (0-15) cm marine sediments of different grain sizes, namely sand, muddy and fine sand, were collected in the western, central and east coast of Algeria, to measure concentrations of natural and artificial radioactivity. The aim of this study is to detect any radioactive contamination, its origin and also to determine the uptake of radioactivity by marine surface sediments.Using a combination of direct gamma spectrometry, radiochemical separations, alpha-spectrometry and beta-counting, activity levels of the most significant naturally-occurring (^{210}Po, ^{210}Pb, ^{226}Ra, etc.) and artificial radioisotopes (^{137}Cs, ^{90}Sr and Pu isotopes) were determined in the samples. The gamma-emitting radionuclides were determined using GeLi detectors and two different geometries, namely, 500 cm^3 Marinelli and 250 cm^3 plastic cylindrical form beakers. For the alpha and beta emitters, after dissolution of the samples, radiochemical separations were undergone. The source of plutonium isotopes was prepared by coprecipitation method on a 0.1 μm pore size membrane filter [1]. Regarding the ^{90}Sr, the chemical recovery was determined by gravimetry and the final source was measured by liquid-scintillation-counting (LSC) [2].

The analysis revealed measurable quantities of artificial radioisotopes,$^{239+240}$ Pu (0.3- 0.6), ^{137}Cs (0.6 - 9), and ^{90}Sr (1.4 - 7.4) Bq Kg-1 dry mass and showed natural radioactivity ranging from (12 - 128), (7 - 28), (5 -35), (5 - 42), (11 -48), (127 - 632), (60 - 131), (52 - 118) Bq Kg^{-1} dry mass, for ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{212}Pb, ^{40}K, ^{210}Pb and ^{210}Po, respectively. The values of the average concentration of radioelements are given in Table 1. Origin of the radioactive contamination, and the uptake of radioactivity by some marine sediments, are discussed and compared with other published data. The ^{137}Cs, ^{90}Sr and $^{239+240}$Pu, in the sediments are clearly observed, and concentration ratios of ^{137}Cs to $^{239+240}$Pu, and ^{238}Pu to $^{239+240}$Pu, which are around 17.5 and 18 respectively, are used to determine eventually their origin. Regarding the uptake of radioactivity, the level is seen to be correlated with the variations of the finest sediments [3] and [4].

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TABLE I. RANGE VALUES OF ACTIVITIES (Bq kg^{-1} DRY MASS) OF SOME ALPHA, BETA AND GAMMA RADIONUCLIDES IN MARINE SURFACE SEDIMENT FROM DIFFERENT BAYS ALONG THE ALGERIAN COAST.

Sampl. Locat.	Date of Sampl.	Nature of sed.	^{226}Ra	^{214}Pb	^{214}Bi	^{210}Po	^{210}Pb	^{228}Ac	^{212}Pb	^{40}K	^{137}Cs	^{90}Sr	^{239}Pu	^{238}Pu
Bay of Ghaza-ouet	1992	muddy	74±23 128±35	10±2 22±4	7±2 ??? 28±6	52±1 118±3	60±2 131±3	29±7 35±8	23±4 26±4	446±85 518±98	7±2 8.5±2	1.5±0.4 7.4±1.4	0.3±0.02 0.6±0.02	0.02±0.01 0.05±0.02
Bay of Ghaza-ouet	1993	muddy	27±3 133±36	8±2 22±4	5±2 28±6	—	—	12±1 35±8	11±1 35±6	184±2 1632±114	0.7±0.1 9±2	—	—	—
Bay of Algiers	1993	Different nature	25±3 66±8	9±1 20±2	8±1 18±2	—	—	7±1 29±3	15±2 41±4	127±24 447±49	0.6±0.3 7.0±1.0	—	—	—
Bay of Zemmouri	1993	Different nature	12±2 63±7	7±1 28±3	6±1 29±3	—	—	5±1 30±4	13±1 48±4	159±15 309±35	0.6±0.1 1.5±0.2	—	—	—

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DISTRIBUTION OF ^{137}Cs IN SURFACE AND DEEP WATER IN THE CENTRAL PART OF ALGERIAN LITTORAL

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A total number of 18 surface and deep seawater samples of volume of 60 l, were collected from 13 stations during september 1997, along the central part of the Algerian littoral; between Algiers (36°49.9N/03°02.3E) and Cherchell (36°39.4N/02°12.4E), covering a distance of 100 Km, *by the Environmental Laboratory, LEIR, on board of M.S. Benyahia laboratory boat (ISMAL).* Among these, 8 surface seaweater samples (2m depth) were collected at a distance of about 4-5 miles from the shore, and the 5 others on a transection reaching a depth of 500 m. The remaining 5 samples were collected at different depths of the water column, ranging from 30 to 350 m. For the surface seawater, the sampling was performed using a pump system, however, for the depth seawater, a 50 l PVC water-bottle sampler was used. The choice of the sampling depths, was based upon measurement of vertical profiles of temperature, salinity and pH, using a multiparameter probe.

The collected samples were analysed to determine the ^{137}Cs concentrations, using the AMP technique [1, 2], and the chemical yield was calculated using the injected ^{134}Cs isotope tracer activity. After chemical pretreatment, the AMP precipitates obtained were transfered to an appropriate plastic container, and oven-dried at 80°C for (24 - 48) h, in order to be counted.

The dried precipitates were analysed by direct counting gamma spectrometry, using a high purity Germanium detector of relative efficiency of 20.6 % and resolution (FWHM) of 1.8 keV at 1332 keV gamma-energy of ^{60}Co.

For the determination of detection efficiency, two standard samples were prepared in the geometries of analysis, using caesium isotope tracers (~ 13Bq).

The results obtained from this work are given in Table 1.

Concerning the surface seawater, the concentrations range from 2.3 to 3.2 Bq.m^{-3}, and the average value is around 2.6 Bq.m^{-3}. After comparison with the litterature [3], it was found that our average concentration value is close to that of Mediterranean Sea in coastal regions. The ^{137}Cs concentrations showed a correlation with the couple (^{40}K activity, salinity), in one hand, and the distance from seashore in the other hand.

The vertical distribution of ^{137}Cs in the water column presents an activity peak at a depth of about 100 m, according to the obtained results, as shown in Figure 1, and seems to be similar to those published for other regions [4]. Moreover, the inventory of ^{137}Cs activity in Bq.m^{-2} in the water column was calculated and compared with the cumulated atmospheric deposition reported for the investigated region [5].

Concerning ^{137}Cs concentration in the transection, a slight decrease is observed and may be due to fine suspended sedimentary materials brought down by Mazafran river in one hand, and the hydrodynamisme conditions when we move away from the coast in another hand. This process can emphasize the uptake of radioactivity by the presence of eddies stream [6] similar to those in our area of investigation. The above variations are illustrated by Figure 2.

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TABLE I: THE ^{137}Cs CONCENTRATION IN THE ANALYSED SAMPLES

Station location	bathymetry (m)	sampling depth (m)	^{137}Cs conc. (Bq.m^{-3})
01	90	surface	3.17
02	65	surface	2.73
03	125	surface	2.58
04	100	surface	2.51
05	100	surface	2.86
06	100	surface	2.37
07	100	surface	2.54
08	250	surface	2.40
09	20	surface	2.97
10	70	surface	/ *
"	"	30	3.25
"	"	70	/ *
12	200	surface	2.61
13	350	surface	2.41
"	"	30	1.97
"	"	100	2.91
"	"	350	2.31
14	500	surface	2.07

* not yet analysed

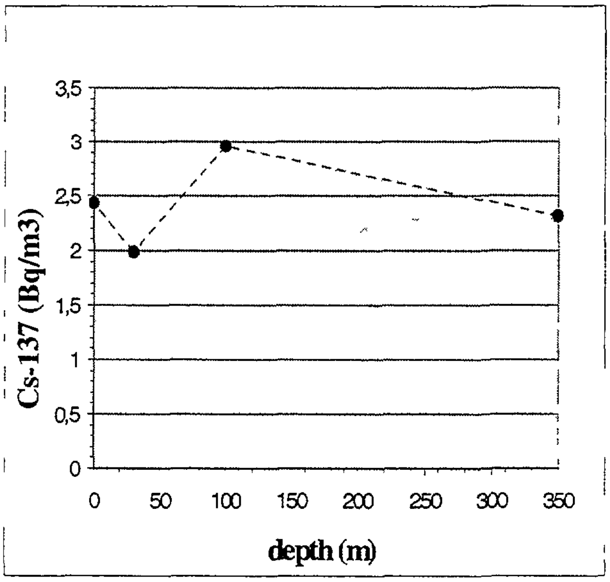

FIG. 1. Variation of ^{137}Cs concentration with depth in the water column

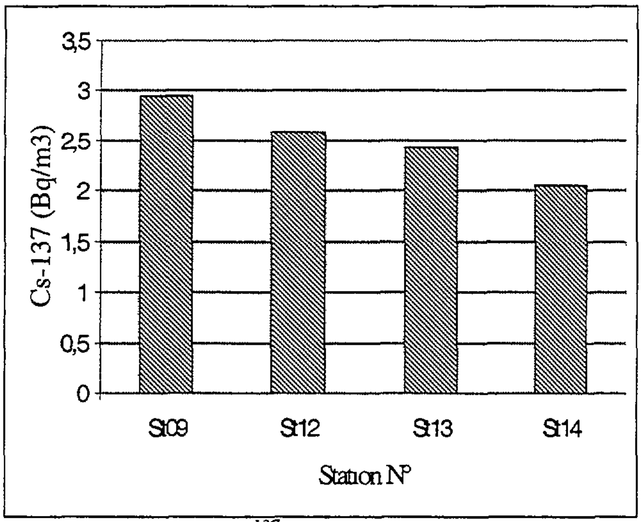

FIG. 2. Variation of ^{137}Cs in the transection

IAEA-SM-354/191P

DISTRIBUTION OF ^{137}Cs IN SEDIMENTS IN XIANGSHAN, XIAMEN AND YANGPU HARBOURS , CHINA

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Xiangshan Harbour (Zhejing Province), Xiamen Harbour (Fujian Province) and Yangpu Harbour (Hainan Province) are tide-channel type bays, located on the southeast coast of China. Six sediment cores were collected in the Harbours in several projects respectively. Sediment samples were collected with a Lehigh gravity corer which utilized a 10.3 cm diameter, PVC core barrel. Styrofoam sediment core retainers were fitted into the top of the core barrel following core recovery to facilitate core sampling without loss of sediment from the barrel. The core barrels were split lengthwise using a circular saw. Following visual inspection for geological parameters (colour, texture, etc.) and photography of the cores, they were subsampled at 1-2 cm or 5cm intervals for the entire length of the core. The sediment samples were stored in air-tight, plastic containers and returned to Nanjing University for ^{137}Cs and other types of analysis. The sediment samples were oven dried at approximately 100 deg. C. at the Nanjing University isotope laboratory and the % loss of water used to determine the wet and dry densities. The contents of ^{137}Cs were counted using an n-type HPGe γ-ray spectrometry system. The coaxial detector has an efficiency of 25%, with a lead shield 12cm thick. Each sample was measured for 12h.

The results of the ^{137}Cs analysis shown that there are recognizable ^{137}Cs peak concentrations and the appearance of horizons in the ^{137}Cs profiles in all 6 sediment cores. . The distribution of ^{137}Cs has a similar pattern in the two cores in same harbour, but there were differences among the three harbours, this reflects the differences in sedimentary environment among the three harbours. In Xiangshan and Xiamen Harbours, four cores(G2, G4, X22, X24) consisted of silt sediment. For the surface sediment ^{137}Cs concentrations ranged from 3.12 Bq/kg to 3.40 Bq/kg(Table I), and the maximum ^{137}Cs activities are between 4.98 Bq/kg to 6.36 Bq/kg (Table I). The surface ^{137}Cs concentrations were about 60% of the maximum ^{137}Cs activities, the relative higher ^{137}Cs concentrations in the surface sediment in these harbours reflect the erosion of ^{137}Cs-contaminated soil particles from the surrounding watersheds transported into the harbours. In Yangpu Harbour, core Y007 was collected in the deepest part of the tidal channel, this core exhibited alternating layers of sands and clays having distinct boundaries. The upper 22 cm of the core contained 55% sand by weight while below this level the sand content decreased to 20%. Core Y004 was collected on the swash platform in the outer harbour where the tidal channel enters into outer bay. This core is distinguished by numerous unconformities and sharp textural changes along its length. The upper 10 cm of the core contained 69% sand by weight. For the surface sediments ^{137}Cs can not be detected (Table I) for Y007 and Y004. The maximum ^{137}Cs activity is 5.33Bq/kg for Y007 and 1.93Bq/kg for Y004. The reduced ^{137}Cs concentration in core Y004 is consistent with the higher sand content(>45%) compare to the sand content (<20%) of cores G2,G4,X22,X24, Y007. These values may be compared with eastern zone of Hong Kong results from [1] (^{137}Cs peak values from 4.7Bq/kg to 6.2Bq/kg at Hebe Haven). Because initial input of ^{137}Cs into the global environment with measurable amounts in sediment was estimated to be around 1950 [2] and the greatest amount of ^{137}Cs fallout was deposited between 1963-1964. If the depth of ^{137}Cs maximum activity was assigned the year 1963 and the depth at which the ^{137}Cs became detectable was assigned the year 1950, the sedimentation rates for these cores can be calculated. Sedimentation rates (Table I) based on the position of ^{137}Cs peak are in good agreement with that based on ^{210}Pb dating [3] and rates based on the occurrence of the horizon are larger than that based on ^{210}Pb dating, this indicates ^{137}Cs may be downward migration in the sediments in these harbours.

TABLE I. SUMMARY OF ^{137}Cs ANALYSES AND SEDIMENTATION RATES DERIVED FROM 1963 AND 1950 MARKER HORIZONS FOR SEDIMENT CORES FROM XIANGSHAN, XIAMEN AND YANGPU HARBOURS

Locations	Station	^{137}Cs (Bq/kg)		Depth to (cm)		Sedimentation rates (cm/a) derived from		
		surface activities	maximum activities	1963 marker horizon	1950 marker horizon	1963 marker horizon	1950 marker horizon	^{210}Pb dating
Xiangshan Harbour	G2	3.12	5.68	34-39	58	1.26± 0.09	1.38	1.20
Xiangshan Harbour	G4	3.40	5.41	45-51	73	1.66± 0.10	1.74	1.73
Xiamen Harbour	X22	3.28	6.36	22-24	42	0.82± 0.04	1.02	0.84
Xiamen Harbour	X24	3.22	4.98	20-22	50	0.75± 0.03	1.22	0.76
Yangpu Harbour	Y004	0	1.93	26-28	53	1.08± 0.04	1.39	1.06
Yangpu Harbour	Y007	0	5.33	36-42	72	1.56± 0.12	1.89	1.52

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TRANSFERT DES RADIONUCLEIDES ^{60}Co, ^{65}Zn ET ^{134}Cs AUX SEDIMENTS ET AUX MOLLUSQUES MARINS EN CONDITIONS DE LABORATOIRE

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Nous avons jugé utile de reprendre et de détailler certaines expérimentations de laboratoire concernant la concentration/élimination de quelques radionucléides importants pour les organismes marins et leur substrat de vie, étant donné que:

- *il existe une variabilité locale des composantes et des facteurs de l'environnement*;
- l'écosystème marin côtier subit une pression d'origine anthropique qui peut lui modifier l'évolution temporelle et même les éléments de structure;
- la teneur de substances et radionucléides de l'eau de mer est instable, avec une tendance d'augmentation qualitative et quantitative plus marquée durant la dernière période;
- le complètement des observations *in situ* et des bases régionales de données contribuent à une compréhension plus claire de l'ensemble des phénomènes, à la délimitation de l'impact anthropogène dans l'environnement, mais aussi au risque humain, assistant, finalement, le processus de décision.

Les expérimentations antérieures effectuées dans le cadre de l'IRRM ont déterminé FC en conditions d'équilibre chez les algues macrophytes *Enteromorpha linza* et *Cystoseira barbata* et chez les mollusques *Mytilus galloprovincialis, Mya arenaria* et *Scapharca inaequivalvis* pour les radionucléides ^{59}Fe, ^{60}Co, ^{65}Zn, ^{85}Sr, ^{89}Sr, ^{131}I, ^{134}Cs ayant les activités situées entre 74 et 222 KBq/L [1].

Les observations ci-devant ont été effectuées sur les mollusques *Mytilus, Mya* et *Scapharca* (organismes entiers et/ou coquilles) et sur certains sédiments marins (Tableau 1), mis en aquariums contaminés uniquement avec des solutions de ^{60}Co, ^{65}Zn et ^{134}Cs, aux activités initiales conformément au Tableau 2. Une partie des expérimentations de concentration ont été continuées avec des études d'élimination des radionucléides (Tableau 2; expérimentations B, D). Le matériel de travail utilisé dans les expérimentations A et B provenait du littoral roumain de la mer Noire, tandis que celui des expériences C et D - de la zone bosphorique de la mer Noire, Istanbul. Les appareils utilisés à l'IRRM (Tableau 1; exp. A, B) consistaient dans une installation multicanal MGS-01 (production IFA Bucarest) et une installation à analyseur multicanal ORTEC-NORLAND 5500 (support AIEA), toutes les deux utilisant des détecteurs NaI (Tl).

Les expérimentations C et D se sont déroulées dans le cadre du course régional *"Strategies and methodologies for applied marine radioactivity and environmental isotope studies for the Black Sea"* organisé sous l'égide de l'AIEA en Turquie (novembre 1994). Les appareils utilisés par le Centre de Formation et Recherches Nucléaires Cekmece d'Istanbul consistait dans une installation à analyseur multicanal CANBERRA 35+ et détecteur NaI (Tl). La durée des expérimentations, les paramètres fondamentaux, les conditions initiales et les principaux résultats sont présentés dans le Tableau 2.

Les facteurs de concentration du ^{60}Co dans les bivalves ont été de l'ordre des dizaines. L'état d'équilibre a été obtenu en quelques jours (*Mya*) jusqu'à 10 jours (*Scapharca*). Le brossage des surfaces externes, la dissection et l'expérimentation sur les coquilles ont prouvé l'existence d'un processus superficiel d'intense fixation, avec la rétention durable à l'élimination en conditions naturelles. La fixation du ^{60}Co sur *le sédiment se réalise surtout dans la couche d'interface, en saisissant un gradient vertical descendant* significatif.

La concentration du ^{65}Zn et du ^{134}Cs chez *Mytilus* a été plus intense dans le cas du premier adionucléide pour de brèves durées. Le tissu mou se distingue par une capacité de rétention relativement plus mportante. Les deux radionucléides peuvent arriver dans le sédiment à K_D de l'ordre de 10^3, mais la valeur éalisée en même temps par le ^{65}Zn a été plus de deux fois supérieure au résultat obtenu pour ^{134}Cs.

TABLEAU I. TYPE DE L'EXPÉRIMENT ET MATÉRIEL ÉTUDIÉ

A. Expérimentation concentration ^{60}Co	B. Expérimentation élimination ^{60}Co
1.*Scapharca inaequivalvis*	1.*Scapharca inaequivalvis*
2.*Mytilus galloprovincialis* (coquilles)	2.*Mytilus galloprovincialis* (coquilles) .
3.*Mya arenaria*	
4.Sédiments littorales	
C. Expérimentation concentration ^{65}Zn et ^{134}Cs	D. Expérimentation élimination ^{65}Zn et ^{134}Cs
1.*Mytilus galloprovincialis*	1.*Mytilus galloprovincialis*
2.*Mytilus galoprovincialis*	
3.Sédiment	

TABLEAU II. PARAMÈTRES ET RÉSULTATS PRINCIPAUX DES EXPÉRIMENTATION EN LABORATOIRE

Exp.	Durée (Jours)	T (°C)	S (%o)	pH	Poids (g±%)	L (KBq/L)	FC (L/Kg)	Tb (Jours)
A. 1.	38	17.5-19	-	-	17.1±21	0.53	14.3±3.4	-
2.	22	18-20.5	14.36	8.5	3.7±22	44.4	74±11	-
3.	21	16-18.5	15.21	5.5	37±36	7.4	20.3±3.9	-
4.	41	18-24	14.7	8	1330	37	7.2±1.4	-
B. 1.	66	18.5-26.5	-	-	17.1±21	-	-	14.5
2.	15	19-23	-	-	3.7±21	-	-	12.6
C. 1.Zn	42h	15	22	-	24.4±13	5.0	21.3±3.9	-
Cs							4.9±0.7	
2.Zn	21.5h	15	22	-	31.4±10	5.0	13.3±2.7	-
Cs							3.1±0.5	
3.Zn	23h	15	22	-	1 g/L	11.1	3150	-
Cs						10.9	1380	
D. 1.Zn	43h	15	22	-	31.4±10	-	-	5.5
Cs								6.1

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IAEA-SM-354/194P

TECHNIQUES NUCLEAIRES ET RESULTATS DU MONITORING ROUMAIN DE LA MER NOIRE DANS LE LABORATOIRE RADIOECOLOGIQUE DE L'INSTITUT ROUMAIN DE RECHERCHES MARINES

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Les investigation préliminaires de radioactivité de l'environnement se matérialisent en mesurages béta global. On utilise deux chaînes de mesure à détecteurs de scintillateur plastique NE 102A f 70x4 mm et ND 304 f 30x5 mm (production GAMMA).

Les analyses gamma de haute résolution se déroulent dans une chaîne à détecteur GeHP à efficacité relative 10%, résolution 2 KeV à 1332 KeV, analyseur multicanal ORTEC-NORLAND 5500, calculateur AST Bravo 386 et imprimante Broteher M-1924L (support AIEA); source et modules NIM.

Les exercices récents d'intercomparaison ont été organisés par IFIN Bucarest (^{137}Cs, ^{152}Eu), AIEA (SD-300, SD-315), le programme régional CoMSBlack (^{137}Cs, ^{90}Sr) et celui bilatéral avec l'Institut de Biologie des mers de sud (IBSS) de Sébastopol, Ukraïne (^{137}Cs, ^{40}K).

Le mesurage avec scintillateurs liquides de ^{3}H et ^{14}C peut être effectué à l'aide de l'installation TRI-CARB 1000 (CANBERRA-PACKARD). Pour la phase liquide on utilise le cockteil ULTIMA GOLD XR (support AIEA, avec l'appareil), tandis que pour les filtres de l'analyise de la production primaire phytoplanctonique, on a procure le cockteil FILTER COUNT.

L'indicateur moyen béta global pour l'eau de mer est, en 1997, de 4.9 Bq/L, ses limites de variation étant 3.3 et 7.5 Bq/L. Les modifications de la salinité influencent les résultats béta global (par le taux differént de ^{40}K), surtout dans le zones de pénétration des eaux douces (aux embouchures du Danube, ou aux déversoirs d'eaux usées dans la zone côtière). Les mesurages comparatifs de l'eau du canal Danube - mer Noire (testé pour l'évacuation des eaux de refroidissement de FENE Cernavoda) ont mis en évidence une valeur béta globale moyenne de 0.19 Bq/L.

Les mesurages béta global des sédiments de la plage ont révélé des valeurs variant entre 30 et 1300 Bq/Kg sec. On a constaté une qualité radiométrique voisine pour les sables de la plage moyenne, du médiolittoral et des sédiments de fond, à < 1 m de profondeur.

Les sédiments submergés présentent des valeurs situées dans l'intervalle 390-1470 Bq/Kg sec. Des valeurs particulières ont été enregistrées devant les embouchures du Danube et sur le couloir de transport des alluvions.

Les algues macrophytes peuvent atteindre des maxima de quelques centaines de Bq/Kg tissu frais (*Cladophora, Ceramium, Bryopsis etc.).* Une moyenne un peu inférieure appartient aux poissons, tandis que les mollusques ont le minimum (en moyenne environ 50 Bq/Kg tissu frais).

La valeur moyenne de la concentration du ^{90}Sr obtenue en 1997 pour l'eau de mer a été de 21 Bq/m^{3}. Un taux relativement maximal de ce radionucléide appartient aux sédiments de fond, ayant en 1997 une moyenne de 4 Bq/Kg sec.

Les organismes marins ont une teneur de ^{90}Sr au-dessous de l'unité. Les poissons sont les plus près de la valeur 1 (en moyenne 0.8 Bq/Kg tissu frais en 1997). Bien que les algues macrophytes ont des concentrations voisines, on observe en 1996 un niveau plus bas. Le tissu mou des mollusques et la forme soluble du radionucléide déterminent leur contenu minimal par rapport aux autres organismes, la moyenne en 1997 étant 0.24 Bq/Kg tissu frais, valeur proche de celle de 1996.

En estimant les valeur d'equilibre des concentrations du radionucléide ^{90}Sr dans les composantes marines, nous avons calculé les suivants facteurs de concentration: poissons - 38, algues macrophytes - 38, mollusques - 12. Le coefficient moyen de distribution dans les sédiments du secteur roumain de la mer Noire est d'environ 190.

L'analyse des échantillons par spéctrométrie gamma a mis en évidence une présence significative d'un autre radionucléide anthropogène, d'intérêt radioécologique: ^{137}Cs.

Le résultat du mesurage d'un échantillon de référence d'eau prélevée au point 44°10'N - 29°15' E Constanta au large) est de 36 Bq/m^3.

La concentration du ^{137}Cs dans le sable des plages touristiques roumaines ne dépasse pas, en noyenne, 5 Bq/Kg sec. On suppose atteindre le seuil avant-Chernobyl après l'an 2000. La diminution de a concentration de radionucléide dans le sable des plages par l'action des processus naturels - autres que a désintegration radioactive - a été estimée avoir lieu en moyenne en $T_{proc} = 10$ ans. L'aménagement des lages avec de grandes quantités des sable de provenance submergée peut conduire à une croissance ocale des concentration de radionucléide.

Les maxima des concentrations des fond dépassent en 1997 aussi 200 Bq/Kg sec. L'apport upplémentaire danubien de radionucléide et de sédiments fins complexes a déterminé la délimitation l'une aire "chaude" devant les embouchures. Les maxima enregistrés en 1997, d'environ 250 Bq/Kg sec à Sf. Gheorghe et à Constanta, c'est non seulement l'effet des conditions locales particulières, mais, dans le lernier cas surtout, la présence d'un phénomène de transport alluvionaire le long du courant descendant N S.

La stratification termo-saline de la masse de l'eau engendre, aux profondeurs qui dépassent 100 n, des concentrations du radionucléide ^{137}Cs inférieurs à 20 Bq/Kg sec dans les sédiments de fond. Dans a partie nord, aux embouchures du Dniester, il y a des concentration minimales (2-:-13 Bq/Kg sec) en ones relativement peu profondes. L'influence de l'apport fluvial sur le niveau des concentrations dans la one de confluence est également remarquée aux embouchures du Dniepr (60-:-189 Bq/Kg sec).

Les calculs effectué avec les donées radiométriques récentes ont étebli le niveau moyen du oefficient de distribution pour le secteur roumain d'environ 2100. La dispersion du résultat, située a 90%, ecommande la valeur indiquée comme orientative, puisque les facteurs locaux ont une forte influence sur e niveau du ^{137}Cs du substrat. Le facteur de radiocapacité, pour des profondeurs de la colonne d'eau allant le 10 à 50 m, varie entre 0.94, respectivement 0.76, pour qu'il atteigne, à la profondeur de 100 m, la aleur 0.65.

Si l'on fait une estimation en condition théoriques, on conclut qu'approximativement une moitié le la quantité de radionucléide pulsée en mer Noire par l'accident Chernobyl se trouve immobilisée sur le ond de la mer jusqu'à la profondeur de 100 m. La capacite de support de l'écosistème marin dans la zone nentionnée est supérieure d'environ 10^4 fois. La plate-forme N-V a la plus grande contribution à la ixation du ^{137}Cs dans cet écosystème, occupant la plus étendue et la moins profonde zone. L'importance le ce fait doit être soulignée aussi parce que c'est ici la partie vitale la plus complexe et dynamique.

Le plus important taux relatif appartient aux poissons avec une moyenne, en 1997, de 2.6 Bq/Kg ec. Les mollusques ont le taux de 1.2 Bq/Kg tissu frais, voisin aux algues macrophytes (1 Bq/Kg tissu rais). Les facteurs de concentration du radionucléide ^{137}Cs sont: 72 pour les poissons, 34 chez les nollusques et 28 aux algues. Le niveau des concentrations du ^{137}Cs en poissons et en mollusques, ainsi ue les valeurs obtenues pour les facteurs de concentration, confirment une fois de plus l'actualité des ecommandations AIEA.

Les mesurages de production primaires dans l'écosystème marin côtier par méthode du ^{14}C sont en rain d'être parachevés. On a poursuivi un cycle annuel. Après les premières essais, il a fallu changer la ecette du scintilateur liquide, à présent les mesurages devant être correlés avec les standards quench et nquench adéquats.

La surveillance du ^{3}H dans l'eau douce peut être faite directement, tandis que pour l'eau de mer il aut la distiller en vue d'éliminer les sels actifs béta. On a en vue ce programme en perspective immédiate, es tests étant déjà effectués.

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MONTE CARLO MODELLING OF THE DISPERSION OF RADIONUCLIDES FROM THE MURUROA TEST SITE

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The Monte Carlo method of simulation of physical processes is a powerful method widely applied in physical sciences. However, it has not often been employed in the modelling of oceanographic processes, although it has several advantages, especially in particle tracking for long distances, as it is computationally more efficient for large scale modelling [1].

The Monte Carlo simulation of dispersion of radionuclides in the marine environment is based on the numerical solution of the three dimensional equation of advection/diffusion (the Langrangian particle tracking technique) [1, 2]. In the presented computations, the advection field used in the simulations was constructed using the mean velocity data obtained from a coupled ocean-atmosphere model [3]. The velocities associated with the transport of a substance relative to a water mass is low (of the order of a few cm/s horizontally and at least one order of magnitude lower vertically). The model is based on the Monte Carlo code developed by J. Ribbe [2].

The decrease of vertical current strength with increasing depth was included in the model. The results of calculations showed high sensitivity to this parameter, which seems to be one of the key variables determining the main features of transport direction and strength of the signal. The temperature and salinity fields were taken from the World Ocean Atlas [4].

The transport processes in the ocean are influenced by a variety of very complex physical, chemical and biological processes. In our calculations, as a first approximation, the chemical and biological processes have been neglected (e.g. sedimentation). We suppose that we are dealing with passive tracers only. Although such an assumption may be correct in the case of tritium only, the aim was to produce concentration fields also for other radionuclides, so the predictions made by compartmental modelling could be checked by the Monte Carlo method.

In the present paper we discuss only the modelling results obtained for the worst case scenario, i.e. a carbonate rock slide with an instantaneous release of radionuclides to the marine environment from underground sources. The estimated releases (in TBq) are 1000 for ^{3}H, 10 for ^{90}Sr and ^{239,240}Pu and 30 for ^{137}Cs. We assume that the total activity is released into the entire water column around Mururoa Atoll. We studied both, the transport of radionuclides as the function of the geographical position, as well as the distribution of radionuclides as the function of horizontal and vertical coordinates. In Fig. 1 we only present, because of lack of space, the results for the first case for ^{239,240}Pu. The change in the spatial distribution of elevations in ^{239,240}Pu concentrations in surface water around Mururoa Atoll can be seen 1, 3 and 5 years after a disruptive event took place. The "radioactive cloud" moves towards the south-east showing only first year concentrations around Mururoa and Tureia (the closest inhabited atoll) of around 100 mBq/m^3, which is about two orders of magnitude above the present background levels. These estimations are in reasonable agreement with the predications of the compartmental models [5, 6].

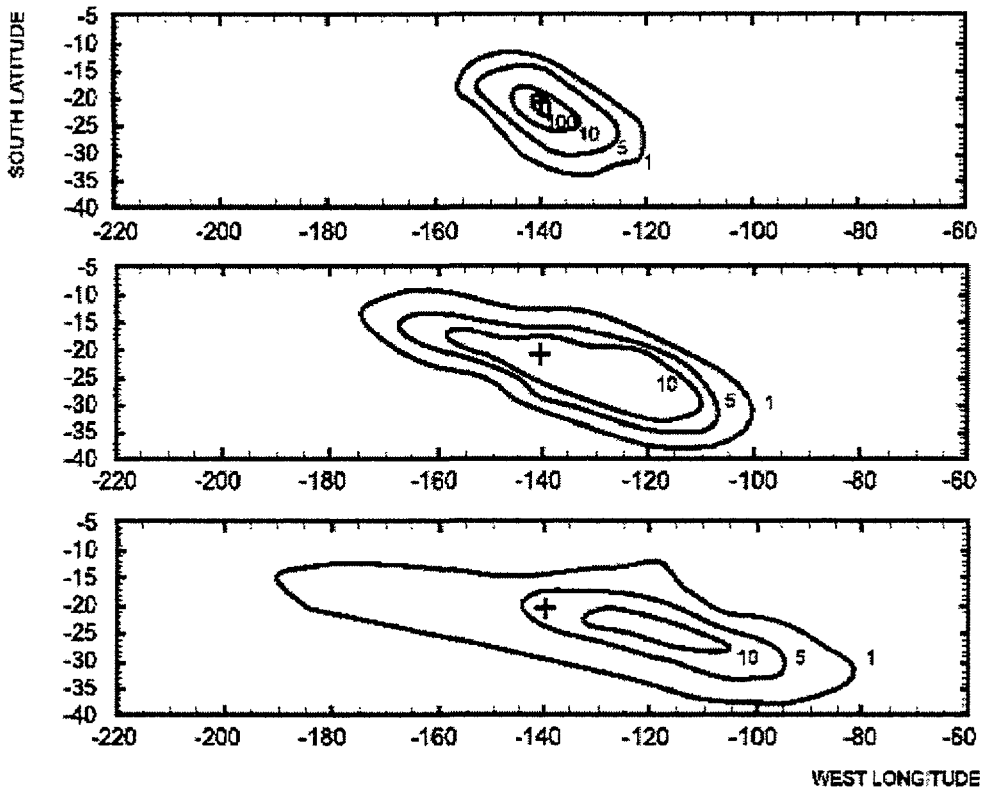

FIG. 1. Spatial distribution of $^{239,240}Pu$ *(in mBq/m*^{3}*) in surface water, one, three and five years after a 10 TBq release (a carbonate rock slide).*

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IAEA-SM-354/197P

RADIOACTIVE CONTAMINATION OF THE GUATEMALAN MARINE ENVIRONMENT

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As part of the IAEA TC project GUA/2/005 "Radioactivity and Contamination of the Marine Environment in Guatemala", concentrations of artificial and natural radionuclides have been determined in marine water and sediments, giving important information to establish the base line of the natural radioactivity and the radioactive contamination in this area that not have been studying.

During July 1995 and July and December 1997 sampling work was performed in 6 stations, located 1 in the Atlantic and 5 in the Pacific Ocean. Fig. 1 Shows the area and sampling stations. Large volume water sampling and seabed sediment was collected in each station.

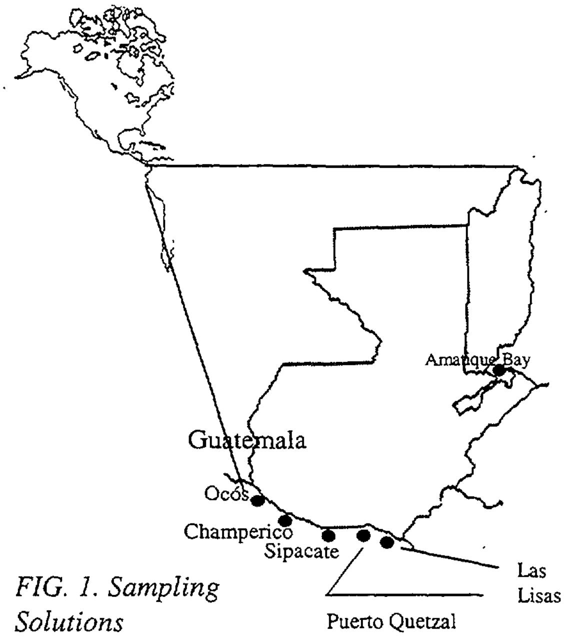

FIG. 1. Sampling Solutions

Table I shows the results obtained of Cesium-137 concentrations in marine water taken during three samplings. Cesium was collected using ammonium molibdophosphate (AMP) to precipitate it, it was dried and measured by gamma spectrometry. The determination of July 1995 correspond to 100 liters of water and 120,000 seconds to meassure, the determination of July 1997corespond to 100 liters of water and 250,000 seconds and the determination of December 1997 correspond to measure of 200 liters of water and 250,000 seconds, wich improved the detection limit and the standard deviation. Although it seems like the concentrations decreased, probably is due to a better destinction between background and area in the gamma spectra, and the uncertainty is given by only standard deviation, (the value of the 1995 sample could be in a wider range); and the Minimun Detectable Concentration (MDC), in 1995 was about 1.2 mBq/L, in July 1997 it was about 0.7 mBq/L and in December 1997 it was about 0.3 mBq/L.

TABLE I. CESIUM-137 IN MARINE WATER (CONCENTRATIONS ARE REPORTED IN MILIBEQUERELS/LITER)

Samping site	July 1995	July 1997	December 1997
Amatique Bay *	1.7 ± 0.3	1.2 ± 0.2	1.3 ± 0.1
Puerto Quetzal **	2.7 ± 0.3	2.5 ± 0.2	2.2 ± 0.1

*Atlantic ** Pacific Ocean (microbequerels/Liter)

TABLE II. SHOWS THE RESULTS OF PLUTONIUM CONCENTRATIONS IN MARINE WATER SAMPLING IN 1995.

Sampling site	Pu- 239+240	Pu-238
Amatique Bay *	19.7 ± 6.7	1.8 ± 0.6
Puerto Quetzal **	4.7 ± 1.6	Not detected

*Atlantic ** Pacific Ocean

Table III shows the results of Cesium-137 in marine sediments. The samples determination of 1995 were carried out using 200 g of sample and measuring during 75,000 seconds. The determination of 1998 were carried out using more sample and measuring by 250,000 seconds. The precision was improved.

TABLE III. CONCENTRATION OD CESIUM-137 IN THE SEABED SEDIMENT SAMPLES (IN DRY WEIGHT) * ATLANTIC ** PACIFIC OCEAN

Sampling site	Cs-137 (Bq/Kg) (1995)	Cs-137 (mBq/Kg) (1998)
Amatique Bay *	8.7 ± 0.5	
Puerto Quetzal **	<1.1	0.46 ± 0.07
Las Lisas **	1.7 ± 0.3	1.09 ± 0.17
Sipacate **	< 0.9	0.22 ± 0.06
Champerico **	< 1.2	
Ocós **	< 1.4	

*Atlantic ** Pacific Ocean

Table IV shows the Plutonium-239+240 and Plutonium-238 in marine sediments, colected in July 1995.

TABLE IV. CONCENTRATIONS OF PLUTONIUM IN MARINE SEABED SEDIMENTS (IN DRY WEIGHT) * ATLANTIC ** PACIFIC OCEAN

Sampling site	Pu-239-240 (mBq/Kg)	Pu-238 (mBq/kg)
Amatique Bay *	663.8 ± 21.7	28.6 ± 2.6
Puerto Quetzal **	164.0 ± 8.1	2.8 ± 1.0
Las Lisas **	347.9 ± 9.7	11.3 ± 1.2
Ocós **	199.8 ± 8.7	8.1 ± 1.4

*Atlantic ** Pacific Ocean

The content of natural radionuclides in the Atlantic Ocean determined by gamma spectrometry are Ra-226, Pb-210 and K-40 which concentrations are 59.9 ± 5.9, 224.5 ± 7.3 and 431.2 ± 10.8 Bq/Kg in dry weight, respectively. The range for Ra-226 in the Pacific sediments is among 33.2 and 48.7 Bq/Kg, for Pb-210 between 101.9 and 151.28 and for K-40 between 291.32 and 356.99 Bq/Kg.

The results show that the sediment of the Atlantic presented the highest concentrations for the artificial and natural radionuclides; which probably is due to the difference between the size particles of both sediments since the Atlantic one shows finer particles and higher content of organic matter due to the location of the sampling site, in the middle of the bay where current is weak and the sediment layer is thick. The Pacific sediments in Guatemala are sandy, so the particles is larger. It is important to remark that the difference between the concentrations of Lead-210 and Radium-226 is much higher in the Atlantic sediment, which seems to indicate that there is a stronger sedimentations process.

The ratio between the concentration of the radionuclides Plutonium-239+240 and Plutonium-238 was always higher than 10:1 wich indicates that the origin of the radioactive contamination in the Guatemalan marine environment comes from the nuclear test and the global accidents, and not from discharges of radioactive wastes as some ambientalist groups claimed are occuring in Guatemala.

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IAEA-SM-354/199P

DISTRIBUTION OF PARTICULATE TRACE METALS ALONG VISAKHAPATNAM COAST (BAY OF BENGAL)

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Particulate trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb), total suspended matter (TSM), and particulate organic carbon (POC) were analysed in the coastal waters of Visakhapatnam (Lat. 7°30'-18°00' N, Long. 83°10' - 83°35' E, Fig.1) along five transects over a period of one year (September1986 to August 1987). Sea water samples were collected with Niskin water samplers (5- lt.) at different depths 10,20,30,40 and 50 m respectively. An aliquot of sample (2- lt.) was filtered through a pre-weighed 0.45 µm, membrane filter (Millipore HA). Filters containing particulate matter were vacuum dried, weighed and subjected to acid digestion (perchloric acid and nitric acid mixture). They were analysed by Perkin - Elmer Atomic Absorption Spectrophotometer (model 2380). Comparison of concentration levels of the particulate trace metals obtained in the present study with those of other coastal and oceanic (euphotic zone) values was shown in Table I.

The range and average concentration of particulate trace metals of Co, Cu, and Pb were found to be relatively high in harbour transect than other (Gangavaram, Lawson`s bay, Rushi hill and Bhimunipatnam) which was due to the impact of anthropogenic inputs (domestic sewage and industrial effluents) into the harbour and their subsequent dispersion into the coastal region. High concentrations of particulate trace metals in the coastal water of Visakhapatnam was also evident from the comparison (Table 1) of overall concentration (range and average) with those of coastal waters of Mediterranean [1] and euphotic zone of world oceans [2]. The impact of particulate trace metal pollution was observed up to a distance of 5 Km from the coast.

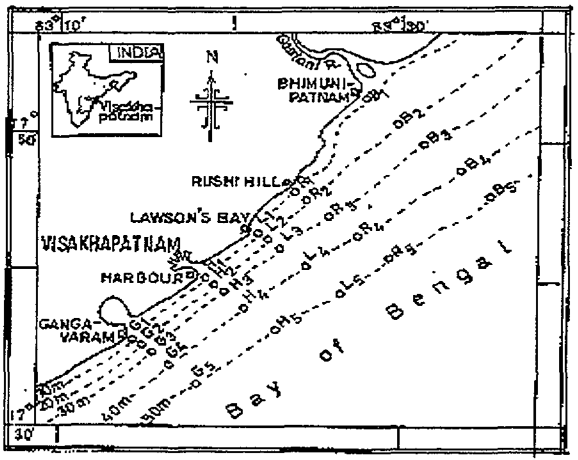

FIG.1. Station locations along Visakhapatnam Coast

TABLE I. COMPARISON OF CONCENTRATION LEVELS OF PARTICULATE TRACE METALS IN COASTAL WATERS OF VISAKHAPATNAM WITH OTHER REGIONS.

Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Present study (nmol. dm^{-3})							
1.50-431	115-5585	ND-98	ND-250	ND-243	8.41-321	ND18	ND-106
(87)	(1810)	(26)	(39)	(52)	(107)	(1.71)	(22)
Present study (µg . g^{-1} , dry wt.)							
5.91-4167	644-47500	644-47500	ND-643	ND-1568	ND-3923	20-3680	ND-340
(402)	(7872)	(107)	(173)	(265)	(528)	(16.3)	(453)
Mediterranean coastal waters [1] (nmol. dm^{-3})							
			ND-41	ND-33	6.21-370	ND-7.1	0.5-64
			(8.5)	(6.3)	(87)	(1.78)	(11.6)
Oceanic values [2] (µg. g^{-1}, dry wt.)							
529		13		200	220		58

Values in parenthesis are averages ; ND = Not detected

Particulate trace metals (Fe, Co, Ni, Cu, and Zn) showed significant positive correlations among themselves and with TSM indicating their close association and common source of occurrence. They are believed to be incorporated in the lattice positions of clays and aluminosilicate minerals. Significant positive correlation was also observed between TSM and POC indicating their common association.

Except Pb, all other trace metals showed an increasing trend from surface to bottom waters, which was attributed either to their precipitation as hydrous oxides (Fe and Mn) or to their scavenging from sea water by hydrous oxides of Fe and Mn, incorporation in phytoplankton or particulate matter (Co, Ni, Cu and Cd). On the other hand, decreasing trend of Pb from surface to bottom was attributed to anthropogenic atmospheric input.

Present study infer that the concentration levels of particulate trace metals in coastal waters of Visakhapatnam were relatively high and needs continuous monitoring so as to assess the health of coastal zone and suggest remedial measures if the levels exceed to hazardous limits.

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IAEA-SM-354/203P

NATURAL AND ARTIFICIAL RADIONUCLIDES IN SOUTHERN OF GULF OF MEXICO MARINE SEDIMENTS

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Preliminary results of quantitative analysis of natural and artificial radionuclides in sediment cores of the uthern Gulf of Mexico (Fig. 1), reveal the presence of 22.01 Bq/Kg ^{226}Ra, 15.56 Bq/Kg ^{214}Bi , 18.17 Bq/Kg ^{214}Pb, .79 Bq/Kg ^{212}Pb, 485.81 Bq/Kg ^{40}K and 2.84 Bq/Kg ^{137}Cs (Fig. 2).

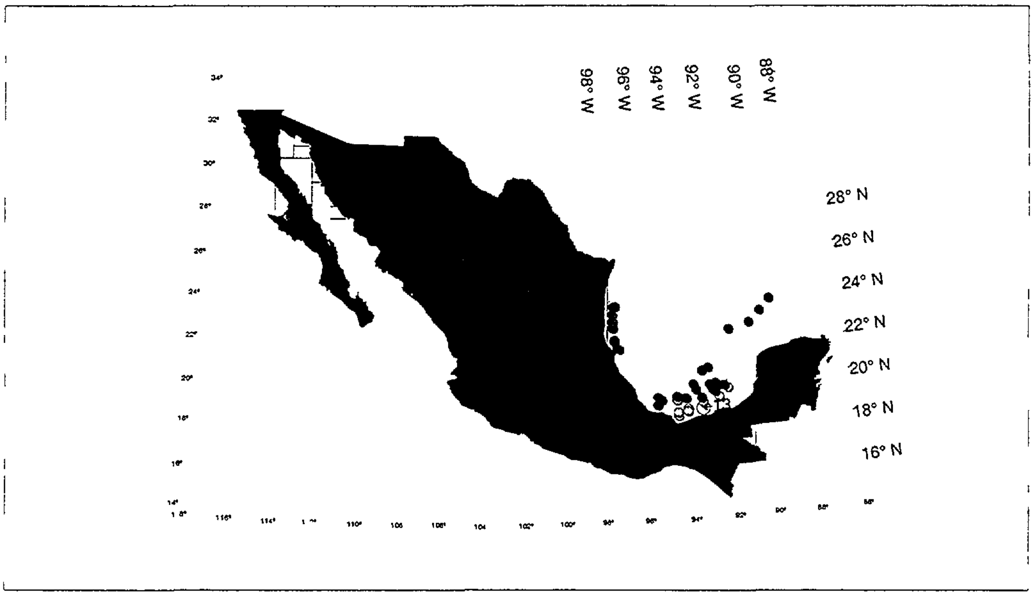

FIG. 1. Sediments samples collected in the Gulf of Mexico during 1993, 1994 and 1995.

These results constitute the first ever sediment radionuclide data sampled in mexican waters of the Gulf of exico. Fifty US Nel Box sediment cores were collected in water depths between 20 to 2000 m in the southern Gulf of exico (GOM). The results presented in this work correspond to the measurements made in the sediment core sampled t station 13 of the OGMEX XII oceanographic survey, during the summer of 1994, at a water depth of 60 m, in the elta of the Grigalva-Usumacinta River, Mexico (Figure 1). The 30-cm deep sediment core was sub-sampled in 2 cm ick slides and frozen for posterior analyses. pH was measured immediately after recovery aboard ship with plane bed lectrode.

Sediment sub-samples were analyzed by XRD to determine mineral composition. The natural and artificial dionuclides were determined with a HpGe Gamma-Spectrometer using a 21000 second counting period, with a ± 8 % ncertainty, (95 % of detection confidence).

cknowledgments

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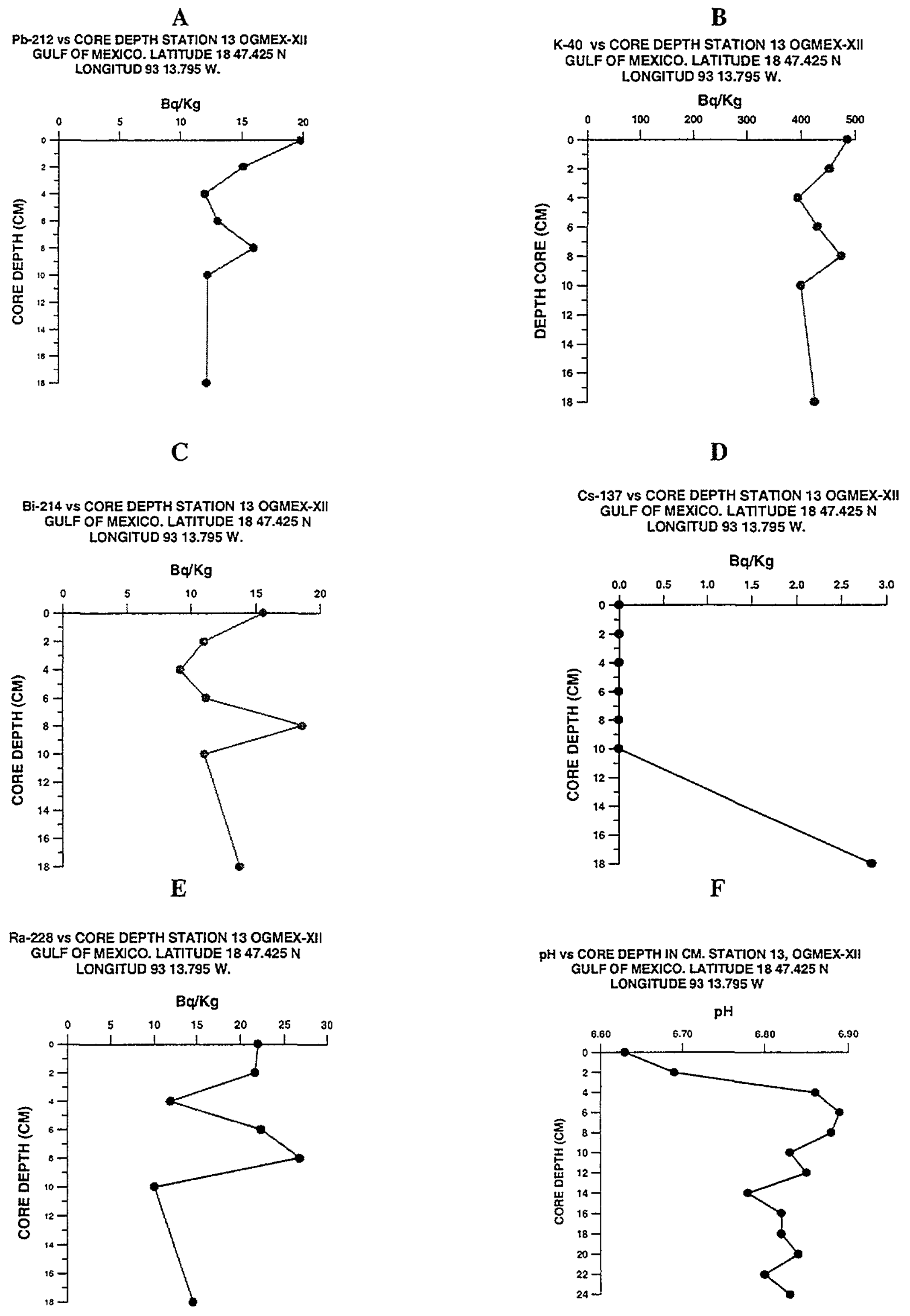

FIG. 2. Profiles of radionuclides concentrations and pH vs core depth of sediment in the station 13 OGMEX-XII in the Southen Gulf of Mexico, latitude 18. 47.425 N and longitude 93 13.795 W. a) ^{212}Pb, b) ^{40}K, c) ^{214}Bi, d) ^{137}Cs, e) ^{226}Ra and f) pH.

TIME-TREND IN THE DEPOSITION OF SELLAFIELD DERIVED PLUTONIUM IN THE NORTHEASTERN SKAGERRAK HIGH SEDIMENT ACCUMULATION RATE AREA.

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A large proportion of the fine-grained material deposited in the Skagerrak and northern Kattegat has been found to originate in western and central Europe, being transported in suspension to the Skagerrak [1]. The highest accumulation rates of sediment have been found to be in the northeastern and eastern Skagerrak [2].

The Surface water exchange of the Skagerrak is dominated by a counterclockwise circulation with water from the North Sea entering the southwestern Skagerrak via the Jutland Current going in a north-easterly direction along northern Denmark. Low-saline water from the Baltic Sea is transported with the Baltic Current northward through the Kattegat into the southeastern Skagerrak where it is mixed with water from the Jutland Current and the resulting current goes mainly northward into the northern Skagerrak. Water is exported out of the Skagerrak into the North Sea and the Norwegian Coastal Current in a southwesterly direction along the south coast of Norway.

There is in other words three possible source terms for radionuclides in the Skagerrak sediments, Sellafield and La Hague reprocessing releases, global bomb test fallout and Chernobyl fallout in the Scandinavian region, especially the Baltic Sea.

Contaminants injected into the western North Sea may however enter the Skagerrak not only via surface water as described above but also via bottom currents. The western North Sea sediments is a long-terra source for suspended matter transported via bottom currents into the Skagerrak. Distinct bottom nepheloid layers have been observed at several stations in the Skagerrak [3].

Recent fluxes of Sellafield derived plutonium isotopes have been determined in a carefully dated (^{210}Pb, ^{228}Th and ^{234}Th) sediment core from the high sediment accumulation rate area in the northeastern Skagerrak. With sediment accumulation rates in the order of 5-kg m^{-2} y^{-1} this region is a major sink for particle reactive pollutants in the North Sea. Integrated ^{210}Pb levels in the investigated core was 15900 Bq m^{-2}, which corresponds to an annual flux of about 490 Bq m^{-2} . This is roughly three times the normal flux in this region.

Although concentrations of plutonium in Skagerrak surface water have decreased substantially during the last 15 years the input of plutonium to these sediments have not changed much, meaning that the main source is resuspended sediments from other parts in the North Sea. The ^{238}Pu/^{239}+^{240}Pu ratios in the upper layers of the core of about 10% clearly shows that Sellafield plutonium is still depositing to a large proportion in the area. It is also clear that the suspended matter carried by the Baltic Current have only small influence on the deposited material in this region although there is a clear Baltic signal in the surface waters. The observed ^{134}Cs/^{137}Cs ratios indicate that only a low fraction of the deposited material originates from the Baltic Sea.

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MODELLING RECEIVING WATER QUALITY RESPONSES TO BRACKISHWATER SHRIMP AQUACULTURE FARM EFFLUENTS

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A monitoring and modelling program was initiated in June 1995 to assess the water quality impacts of brackishwater shrimp aquaculture. India in recent years has been second to China in world wide shrimp aquaculture production. The economic benefits. however, are accompanied by several reports of the environmental damage caused by aquaculture. When this project was initiated, a major concern was the loss of the crop due to the outbreak of shrimp diseases that virtually wiped out the production along the East Coast of India with an estimtated loss of US$ 70 million. This monitoring and modelling program was designed to assess the water quality. Impacts from brackish water shrimp aquaculture farms on an estuary located near Vishakapatiiani, in Andhra Pradesh, India.

The objective was to perform a waste load allocation and determine the extent of aquaculture that the creeks can sustain, by meeting the water quality criteria for both the creek ecosystem and pond culture. Based on these results, similar assessments may be performed for other sites supporting large scale aquaculture activities. This paper introduces the sampling program and modelling methodology of the study.

The study area has 21 farms with 194 hectares (ha) of land utilised for brackishwater aquaculture with 97.7 ha intensive, 93.9 ha semi-intensive and 2.8 ha extensive. The farm sizes range from 26.4 ha to 2.8 ha. The five largest farl~ls occupy 104 ha (53.5%) of the farmed area and four of these farms practice semi-intensive farming. Since the disease of 1994, 19 farms (183 ha) have been disinfecting the influent water in reservoir ponds prior to utilisation in the tanks. The ponds currently exchange 25 % of the water once in a week. The previous practice was to exchange water everyday. There is no treatment of the effluents.

The water quantity and quality data was collected from the 9 creek avatar quality stations (WQS) and the 10 pond stations once every fortnight during high and low tides. Three crop cycles have been sampled. The period between the crops was also being sampled at the same frequency. Typical crop periods are 4 months in duration, thus resulting 8 sampling days per crop. There have been 30 synoptic sampling days covering the creeks and pond effluents.

Each station has a tide pole referenced to the chart datum for stage measurements. The fortnightly. water quality monitoring program at high and low tides in the creeks measures of' temperature, salinity, Dissolved Oxygen. Turbidity. Total Suspended Solids. BOD, dissolved nutrients (amonia, nitrite, nitrate and phosphate) and hydrogen sulphide; and microbiological parameters (total *bacteria, total vibrio, total coliform and salmonella). Samples are also taken of the bottom sediments for* microbiological parameters. In addition, three surveys are carried out for twenty four periods with samples taken every four hours for all the parameters listed above. The three 24 hour surveys are used for calibration and validation of the model. The fortnightly observations are used for validation of the model run in the continuous mode.

Farm sampling for the chemical and microbiological parameters was similar to the creek sampling while the physical data includes farm and pond size, feed and pond management characteristics, and volume of influent and effluent. Additional data on the freshwater inflow, tidal regime, land use characteristics, precipitation and atmospheric temperature is derived from several govemment agencies. All data collection adheres to standard procedures [1] with a QA7QC document prepared for this project.

The modeling component includes the calibration and validation of a two dimensional finite difference model for hydrodynamics and water quality (WQMAPW) developed by Applied Science Associates (1996). The model adopts a boundary-fitted coordinate approach. It contains a grid generation program that uses a set of quasi-linear elliptic transformation equations. The hydrodynamic model utilises continuity and momentum equations, solved in the curvilinear coordinate system. For dissolved oxygen and microbiological parameters, WQMAP utilises WASPS kinetics [2]. The model utilises a simple GIS interface, ASAMAP for decision support , and pre and post processing of the model.

At the current rate of activity, there are violations of the Dissolved Oxygen criteria in the receiving waters for approximately two hours in the early dawn period. Initial analysis of the water quality data suggests a direct relationship between dissolved nitrate and bacterial concentrations with production, for the upstream station of the Malagedda, where the flushing time is the longest. However, since this observation is based on a ssingle season production data verification is essential.

The modeling for the hydrodynamics of the creeks has been performed with typical with an average error of 0. 1m for the high and low tide. Preliminary modeling for the water quality was begun with bacterial concentrations of total coliform and vibrio counts, based on the assumption that shrimp production is the cause for high bacterial counts in the receiving waters. Using average effluent concentrations as inputs from the shrimp farms, modeling of scenarios suggest the obvious that a common effluent treatment plant with a disposal point near the open boundary would significantly decrease bacterial concentrations in the creeks.

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CONTEXTE MEDITERRANEEN DE LA CIRCULATION DES EAUX LE LONG DES COTES TUNISIENNES

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La force principale qui contrôle la circulation générale des masses d'eau en Méditerranée résulte de son caractère de "bassin de concentration". Par différents mécanismes thermodynamiques (évaporation, transports, formation d'eau profonde en hiver,....) la Méditerranée fabrique une eau relativement dense qui occupe 70% de la totalité du bassin [1] pour finalement s'écouler vers l'Atlantique. Les flux de sens opposés dans le détroit de Gibraltar sont dus à des gradients horizontaux de pression dirigés vers la Méditerranée dans la couche de surface et vers l'Océan dans la couche profonde.

L'évolution spatiale de la densité sur la verticale montre un mouvement généralement orienté vers l'Est dans les couches de surface, alors que, dans les couches intermédiaires, le mouvement dominant est dirigé vers l'Ouest. Cependant, la force de Coriolis tend à générer des trajectoires cycloniques dans les différents sous-bassins, commençant par le détroit de Gibraltar pour les eaux de surface, par le bassin nord-est Levantin pour les eaux intermédiaires, et finalement par les différentes sources d'eaux profondes (Golfe du Lion par exemple) pour les eaux profondes. Mais il y a des exceptions notables à ce schéma, en particulier dans les eaux de surface: des gyres anticycloniques existent à l'ouest de la Mer d'Alboran, en plusieurs endroits le long de la côte algérienne, dans le Golfe de Syrte. De plus, plusieurs tourbillons existent dans la partie centrale des différents bassins, et en particulier dans le bassin Ionien.

Les vents, cependant, très irréguliers dans leur intensité et dans leur distribution spatiale et temporelle influencent la circulation générale, en particulier, dans les régions sur lesquelles soufflent des vents forts et réguliers: la "*Tramontane*", par exemple, occupe un rôle majeure sur la partie ouest du Golfe du Lion et le long de la côte nord-est de l'Espagne.

La salinité de l'eau atlantique croît à mesure qu'elle progresse vers l'Est pour parvenir aux côtes du Moyen-Orient. L'eau chaude et salée que l'on rencontre à la surface entre les îles de Rhodes et de Chypre à la fin de l'été, connaît une intense évaporation suivi d'un refroidissement en hiver dû aux vents secs et froids émanant des hauts plateaux de Turquie. Ces effets atmosphériques induisent des mélanges dans les 150 à 200 premiers mètres, dont il résulte la formation d'une masse d'eau type: l'eau Levantine (T=15.7°C, S=39.1, s_t =29,00) qui s'écoulent dans tout le bassin Est autour de 300 mètres de profondeur. Cette eau intermédiaire se dirige lentement vers l'Ouest. Au moment ou elle traverse le Canal de Sicile, affectée par les mélanges avec les eaux adjacentes, ces caractéristiques moyennes sont alors T=14.0°C, S=38.75. Cette eau alimente le bassin Ouest en rejoignant le mouvement cyclonique de la circulation générale à une profondeur intermédiaire juste au dessous l'eau Atlantique et dessus de l'Eau Profonde.

L'organisation globale de cette circulation correspondant aux caractéristiques décrites ci-dessus confèrent au bassin, en vertu des lois de l'hydrodynamique, une dissymétrie Nord-Sud en particulier dans bassin occidental. En effet, la circulation est très turbulente le long du continent africain et relativement stable le long du continent européen. D'un côté, la turbulence accélère la dispersion des polluants et des nutriments et favorise en particulier un développement relativement important de toute la chaîne alimentaire. De l'autre côté, une circulation faiblement énergétique est peu favorable pour le développement des processus biologiques et pour la dispersion de produits polluants.

Les grands traits du cheminement de l'eau d'origine atlantique sont globalement bien représentés sur les schémas les plus courants [2]. Le problème résident dans la forte variabilité spatiale et temporelle qui caractérise cet écoulement et dont l'estimation est souvent biaisée. Cette variabilité se manifeste, en particulier, par deux types de phénomènes, les zones frontales et les structures turbulentes de moyenne échelle. Autrement dit, la circulation générale réelle n'est pas à l'image des lignes de courant se contractant dans les détroits ou s'épanouissant dans les bassins successifs; les courants qui animent les eaux superficielles sont fortement instables, forment des méandres qui génèrent des tourbillons, qui peuvent venir ensuite interagir avec eux.

La circulation de l'eau d'origine atlantique, entre le Détroit de Gibraltar et le canal de Sicile, présente des caractéristiques fondamentalement différentes selon que l'on se trouve au large des côtes marocaines, algériennes ou tunisiennes. A l'ouest, cette circulation est relativement stable et étroitement liée à la géomorphologie du détroit de Gibraltar et de la mer d'Alboran. A la sortie de cette mer, la circulation est, généralement, dirigée des côtes espagnoles (2°W) vers les côtes algériennes (1°W); cette circulation prend ensuite la forme d'une veine de courant qui coule vers l'Est le long de la côte africaine et devient généralement instable à partir de 1-2°E [3]. Des méandres puis des tourbillons cycloniques et anticycloniques se développent; les tourbillons dérivent vers l'Est à des vitesses de quelques cm.s^{-1}, mais seuls les anticycloniques croissent jusqu'à atteindre un diamètre de l'ordre de 100 km). Ils s'éloignent ensuite de la côte et sont parfois repérés sur des thermographies pendant plusieurs mois, ils peuvent alors atteindre des dimensions de plus de 200 km et revenir vers la côte pour interagir avec la veine de courant [4].

Le canal de Sardaigne est la région la moins étudiée de la Méditerranée occidentale. Néanmoins, des résultats plus récents basés sur l'analyse des données de la campagne MEDIPROD5, [5] suggèrent qu'une partie de LIW coule vers l'est le long du talus algérien, ce qui contredit les résultats de [6]. Il est tout à fait plausible de penser que la circulation des eaux qui est généralement parallèle à la côte tunisienne peut certainement lui devenir perpendiculaire en présence d'un tourbillon, et entraîner à la côte des mouvements verticaux qui influenceront directement la distribution des sels nutritifs et de la biomasse phytoplanctonique. Ces tourbillons entraînent l'eau d'origine atlantique des côtes algériennes vers le large, leur influence pouvant se faire sentir loin vers le nord. En revanche, leur progression vers l'est est empêchée par le développement du plateau continental le long des côtes tunisiennes. Ils perturbent ainsi la circulation de l'Eau Levantine Intermédiaire [7] s'écoulant à partir du bassin Est.

La description précise de la dynamique des masses d'eau au large des côtes tunisiennes demeure donc assez peu précise. Les récentes données hydrologiques collectées dans la région clé que constitue le canal de Sardaigne et le détroit de Sicile ont permis de mieux décrire les principaux phénomènes qui prévalent dans cette région et qui affectent la circulation à l'échelle de toute la Méditerranée. Ainsi, l'intense variabilité à moyenne échelle qui caractérise le détroit de Sicile constitue un des principaux résultats auquel l'analyse de ces données a permis d'aboutir [8].

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DISTRIBUTION OF ALIPHATIC AND AROMATIC HYDROCARBON IN DATED SEDIMENT CORES OF THE GULF OF THAILAND

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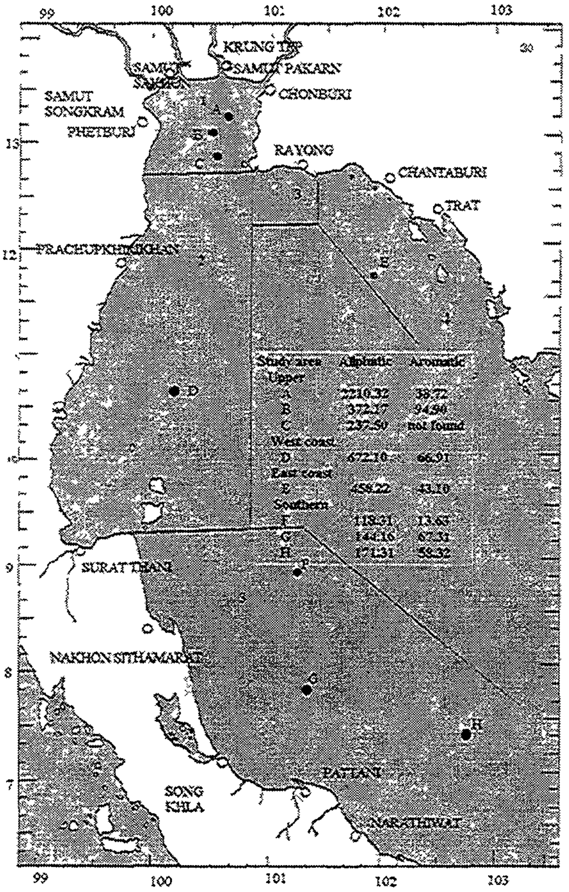
Oil pollution from shipping accident is the most outstanding and chronic ones for marine environment. Tanker operations and leakages from production platforms also have been thought to be the major sources of oil pollution in the sea. Therefore,for many years most of the studies have devoted to contaminations from these sources i.e. the studies to clean up of oil slicks, assessment of environmental impacts, recovery of oil-polluted natural resources as well as co-operative to establish protective measures. Up to now, we can say that these circumstances can be controlled at some level. There is also realization that these circumstances always occur in the deep sea which have a large dilution capacity due to the large volume of sea water, accordingly, they can hardly affect the coastline. In addition, many studies reported that oil pollution in marine environments from human acitvities have much decreased during the last 10 years.

Recently, many scientists have turned their attentions from those major sources which affect very limited areas to small but routine discharges from land-based sources which can accumulate and cause a long term effect on the environment.

In this study sediment core samples from 8 stations in the Gulf of Thailand were collected during September 1992- August 1994. The sample sites were chosen in the followings (Fig 1) : Upper Gulf of Thailand, near Chao Phraya River mouth (very high risk area), Upper Gulf of Thailand down to Ban Don Bay, Surat Thani (high risk area), along the coastal area of Rayong, Nakhon Srithamarat and Phuket Island (medium risk area), and along the coastal area of Chantaburi and Trad province (low risk area) [1] .

Sediment cores have been dated by ^{210}Pb dating method [2]. Aliphatic and aromatic hydrocarbon have been analyzed by GC and GC/MS technique. Total n-alkane in surface sediment were 0.237 - 2.210, 0.672, 0.458, and 0.118-0.171µg/g dry weight with the average of 0.940, 0.672, 0.458, and 0.144µg/g dry weight for area 1,2,4 and 3 respectively.



Study area	Aliphatic	Aromatic
Upper		
A	2210.32	38.72
B	372.17	94.90
C	237.50	not found
West coast		
D	672.10	66.91
East coast		
E	458.22	43.10
Southern		
F	118.31	13.63
G	144.16	67.31
H	171.31	58.32

Fig 1 Sampling locations in the gulf of Thailand indicated area 1 is very high risk area, area 2, high risk area, area 3, medium risk area and area 4, low risk area (Rungsriangsan, 1989 (in Thai))

Total n-alkane in surface sediment in area 4 were higher than those in area 3 eventhough area 4 was considered as the lowest risk area probably due to the development of industrial complex along the east coast(Rayong, Chantaburi and Trad provinces). Comparison of total n-alkane in the Gulf of Thailand showed the high value at the station near-shore and tend to decrease with the distance away off-shore.

Hydrocarbon contamination was found in near-shore sediments particularly around industrial and urbanized sites. Source of contamination has been studied based on several methods i.e. chromatogram characterization, UCM study, LMW/HMW ratio [3] n-C16 ratio [3,4] (Carbon preference index (CPI) [5], C17/pristane ratio [3] , C18/phytane ratio [3] and pristane/phytane ratio(4). It is concluded that hydrocarbon found in near-shore sediment derived from both biogenic (phytoplanktons and higher plants) and anthropogenic sources. In off-shore area, hydrocarbon were mostly from biogenic sources particularly from phytoplanktons. This indicated that fallout on to land and transport of with terrigenous particles from the drainage basin is more important source of hydrocarbon contamination than fallout directly into the Gulf.

The aliphatic hydrocarbon concentrations decrease with respect to depth in all cores. UCMs have been found at 0-22, 0-16, 0-12 and 0-10 cm depth layer at station A, B, D and E,respectively. By using sediment dating technique, it is concluded that contamination of aliphatic hydrocarbon from pyrogenic sources were found at much earlier date at station near-shore (1940AC and 1947AC at station A and B, respectively) when compared to station off-shore (1981AC and 1960AC at station D and E respectively). Thailand's first import of kerosene is 100 years ago during King RamaV reign [6].

Total n-alkane concentrations correlate with depth and organic carbon concentrations in sediment samples. Therefore, the regression equations to predict total n-alkane concentration in sediment samples can be formulated (Table I).

TABLE I. REGESSION EQUATIONS TO PREDICT TOTAL N-ALKANE CONCENTRATION IN SEDIMENT OF THE GULF OF THAILAND

Study area		Regression equation	R^2
Upper Gulf -	A	-45.93+1293.36(OC)-10.05(D)	0.81
	B	98.65+87.92(OC)-10.54(D)	0.90
	C	185.04+80.32(OC)-5.47(D)	0.91
East Coast	D	903.07-351.62(OC)-16.86(D)	0.74
West coast	E	72.22+355.43(OC)-3.89(D)	0.26
Southern	F	69.81+62.83(OC)-0.35(D)	0.21
	G	-44.06+403.72(OC)-0.10(D)	0.32
	H	274.46-230.60(OC)-2.45(D)	0.76

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RELEASE AND TRANSPORT OF ARTIFICIAL RADIONUCLIDES FROM NUCLEAR WEAPONS RELATED ACTIVITIES IN THE OB RIVER, SIBERIA OVER THE COURSE OF THE NUCLEAR AGE

XA9952066

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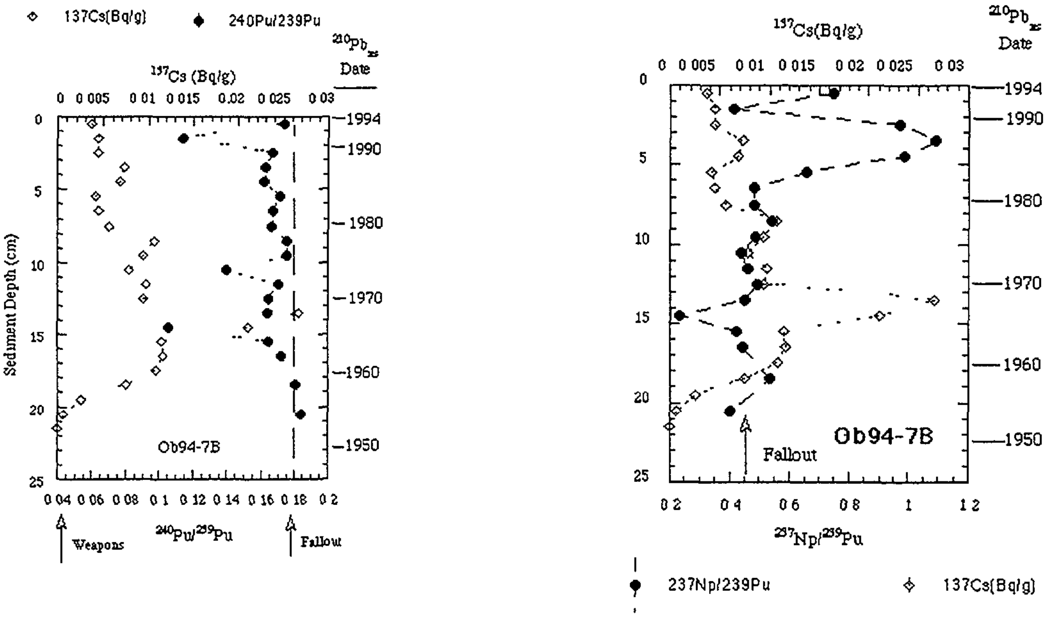
Studies of sediment cores from lakes on the flood plain of the Ob River, Siberia have been used to develop a history of the release, transport, and deposition of artificial radionuclides related to the development and testing of nuclear weapons over the duration of the nuclear age (~1950 to the present) in this major Arctic river system. The Ob is of particular importance in this regard as two of the former Soviet Union's major weapons production plants, Mayak and Tomsk-7, and the Semipalatinsk test site are located within the Ob drainage basin. Accidents and intentional releases of radionuclides at both plants have been substantial, raising the issue of transport throughout this extensive river system as well as delivery to the Arctic Ocean. Our studies have included determining sediment profiles of ^{239,240}Pu, ^{137}Cs, and the natural nuclide ^{210}Pb and its parent ^{226}Ra in a number of cores from the Ob delta, as well as analysis of ^{239}Pu, ^{240}Pu, and ^{237}Np. The latter provide sensitive measures of the presence of non-fallout materials derived from weapons production activities.

Results presented to date have demonstrated that high resolution records of deposition of nuclides are preserved in the Ob sediments from many of the lakes sampled. In addition, we have concluded, primarily on the basis of ^{239,240}Pu/^{137}Cs and ^{238}Pu/^{239,240}Pu ratios, that the dominant source of ^{239,240}Pu and ^{137}Cs in the sediments of the Ob delta is global fallout from the atmospheric nuclear weapons tests of the late 1950s and early 1960s [2]. However, there are several clear isotopic signals that cannot be attributed to global weapons testing fallout. Analysis of ^{239}Pu and ^{240}Pu by mass spectrometry in one core indicates that the ratio ^{240}Pu/^{239}Pu is close to but frequently below that expected for global fallout over the period 1950-1994. However, in three horizons this ratio falls sharply toward values expected for weapons grade material and the ratios reported by [1] for contaminated soils at both the Semipalatinsk test site and the Mayak area (Figure 1a). Based on an assumed weapons grade ratio of .04, as much as half of the Pu in these horizons is derived from non-fallout sources, with a deposition event as recent as the early 1990s. The sharpness of the peaks with low ^{240}Pu/^{239}Pu suggest rapid transport with little mixing along the river, a remarkable conclusion given the distance of ~1700 km from possible sources at the weapons plants. In the same core, the ratio ^{237}Np/^{239}Pu is indistinguishable from that expected for fallout prior to ~1982; the ratio then increases sharply, reaching maximum values in the late 1980's, but continuing at elevated values to at least 1994, the sampling date (Figure 1b), indicating a persistent non-fallout source for this nuclide. The ^{237}Np is not related to the elevated ^{239}Pu horizons and hence must represent an independent source.

Sediment cores from the mid-reach of the Ob River, including the Ob, the Irtysh, and the Tobol have been analyzed to investigate the nuclear contaminants, noted above, closer to the presumed sources as well as to establish the source locations. The plants and test site are each located on a different section or tributary of the Ob and hence studies in this area can provide a clear definition of source. In addition, many of the cores from this area of the river have accumulation rates in excess of 1 cm/yr and provide an opportunity for resolution of contaminant events on an annual scale. Analyses of ^{137}Cs profiles in these sediments indicate a substantially more complex record as compared to those of the delta. The profiles are still dominated by the large maximum in ~ 1965 that we continue to associate with the global fallout maximum (Figures 2a, 2b). In both cores 10 and 11 (Tobol and Irtysh rivers, respectively), there is a strong ^{137}Cs peak well above the fallout period, dated at ~ 1986. The timing and co-occurrence in both

The ^{137}Cs is shown for reference and is indicative of the deposition of global fallout. Isotopic ratios for fallout and weapons grade material (Pu) are also indicated.The chronology is derived from excess ^{210}Pb. rivers indicate a common source which we suggest is Chernobyl. This is further supported



1a. 1b.

FIG. 1 a.) Sediment profile of ^{137}Cs and ^{240}Pu/^{239}Pu collected in the Ob delta. b) the depth Profile of ^{237}Np/^{239}Pu in the same core.

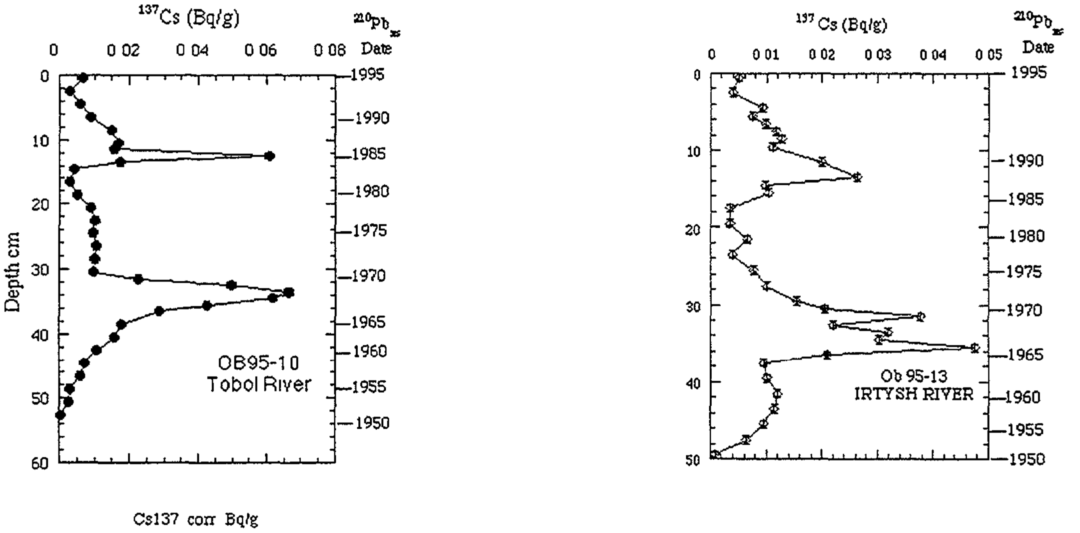


FIG. 2 Profiles of ^{137}Cs in sediments of the mid-reach of the Ob River drainage. Sediment chronologies are based on excess ^{210}Pb analyses.

by the absence of a Pu enrichment, and, especially, the presence of ^{134}Cs, which requires a relatively recent event ($t^{1/2}$=2.06 yr.). One of the cores from the Tobol River (Mayak is in its drainage area) contains a very deep (70 cm) ^{137}Cs peak below what appears to be the usual fallout peak, raising the possibility that it is related to the early Mayak releases to the Techa River. The excess ^{210}Pb profile is, however, quite complex rendering the chronology of this core uncertain. Establishing the origin of this and a number of other features in the ^{137}Cs profiles requires the complementary Pu and Np data.

Analyses of the ^{239}Pu, ^{240}Pu, and ^{237}Np of the sediment cores are currently being done by newly developed ICP-MS instrumental methods. The ^{239}Pu and ^{240}Pu data, particularly the ^{240}Pu/^{239}Pu ratio, complement the ^{137}Cs data by clearly identifying fallout and non-fallout materials. As noted above, the

$^{137}Cs/^{239,240}Pu$ ratio is also a very useful identifier of fallout vs. non-fallout sources. Thus the sensitivity of the $^{240}Pu/^{239}Pu$ ratio to weapons grade material and the $^{137}Cs/^{239,240}Pu$ ratio together make it possible to identify nuclides released from the nuclear facilities in this watershed that are significantly different in their proportions from those characteristic of fallout, and to track the transport of the nuclides along the rivers sampled. In addition, ^{237}Np data from these cores should make it possible to identify the geographic source area for this nuclide and hence the facility(ies) from which it originates. This paper will present the results of ^{239}Pu, ^{240}Pu, ^{237}Np, and ^{137}Cs analyses, within the context of the chronologies of sediment deposition, for three cores from the mid-reach area of the Ob River (Ob, Irtysh, and Tobol Rivers) and the implications for weapons related radionuclide releases and transport in this major Arctic river system.

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RADIOCAESIUM-137 IN SOME MARINE SPECIES IN COASTAL ZONE OF LIBYA (SIRT GULF)

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The *main source of artificial radionuclides in the* Mediterranean *sea have been the* testing of nuclear weapons and the discharge of nuclear power stations.

^{137}Cs is a very abundant, fission product, with a half-life of about 30 years. Its production in nuclear weapons detonations has resulted in world distribution through the biosphere and its mobility and physiological properties have led to detectable activity concentrations in essentially all organisms. ^{137}Cs is potentially significant contributor to the radiation dose to man. Because of its abundance, long physical half-life and biological mobility, ^{137}Cs is a critical component of the nuclear fuel cycle (Whicker et al., 1972 & Pendleton et al., 1965). ^{137}Cs was initially found as a soluble cationic species in surface sea water, fromwhere it slowly migrated to deeper layers (Bowen & Sugihara, 1961; Bowen & Roether, 1973). In this article we present our measurements on the fish, sponge, sea weeds, sea grass and sea water activity concentration of ^{137}Cs in coastal zone of Libya (Sirt gulf).

Sampling procedure: Fish, sponge, sea grass and sea weeds were washed in distilled water, dried, broken to remove sea residules, ashed in nickle crucible for 24 hours at 450 ^{0}C and cooled at room temperature in dissicator.

Sea water filtered and radiocaesium-137 was precipitated by addition of NaOH and NH_4Cl added as buffer to hold magnesium in solution and the volume of the sample were between 100 and 200 liter (Johns, F. B. et al., 1979).

Measurement of radioactivity: All activity concentrations of these samples were measured using a (SEN-ELECTRONICS) low-level gamma counting system consisting of a high-resolution, HPGe detector coupled to a 8192-channel analyzer. The energy resolution of the 1332 KeV line from ^{60}Co was found to be 2.1 KeV at full width of half maximum (FWHM) with the relative efficiency of 30% .

The activity concentration of ^{137}Cs in the sea grass, sea weeds, and fish are shown in Table I. As the number of samples was not large enough to determine the underlying frequency distribution, each group was characterized by the mean and the corresponding S.D.

TABLE I. ACTIVITY CONCENTRATIONS OF ^{137}Cs IN SOME MARINE SPECIES IN SIRT GULF OF LIBYA.

Sample	Activity concentration (mBq kg^{-1})
Sponge	1590 ± 364
Sea grass (Padina Pavonia)	1440 ± 386
Sea weeds (Cistozira)	1320 ± 362
Fish (Sciena Cirrhosa)	185 ± 4.8

The average surface sea water fallout ^{137}Cs activity concentrations in the coastal zone of Libya (Sirt gulf) have varied. The variations in surface sea water activity concentrations are due to differences in the rates of new atmospheric fallout to the Mediterranean sea and to process moving caesium laterally and to depths in the water mass.

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XA9952068

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RADIONUCLIDES AND HEAVY METALS AS TRACERS OF THE EASTERN BLACK SEA CONTAMINATION HISTORY

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The studies were made in sediment cores recovered during joint russian-american expedition on board of R/V "Rift" (March, 1993) from both Caucasian shelf and continental slope (Fig. 1) using gravity corer, 62 mm of inner diameter, 1 m length, fitted with acrylic liner. The cores were extruded in vertical position and sectioned into 1 cm intervals to 10 cm, 2 cm intervals below this depth. Cs-134 and Pb-210 were analysed in ORNL with help of low energy gamma-ray spectrometry. Toxic heavy metals (Cu, Pb, Zn, Cd, Hg, Co, Ni) were studied in SBIORAS by atomic absorption method. Age calculations were made using model of the constant flux of Pb-210 [6].

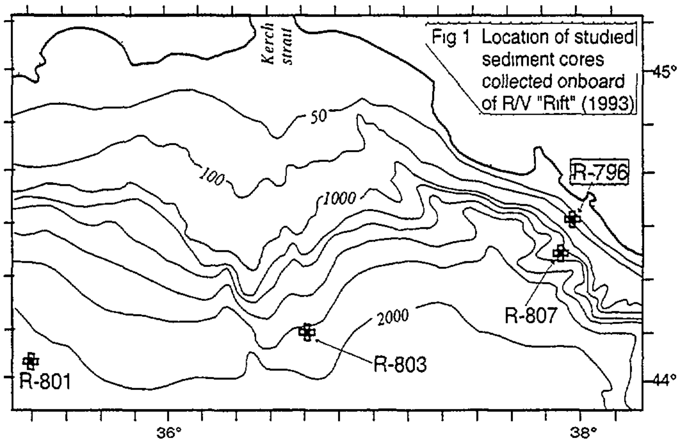

Fig 1 Location of studied sediment cores collected onboard of R/V "Rift" (1993)

Radionuclides. Analysed cores indicate the highest levels of cesium-137 in the sediments at shallow station R-796-3 (depth is 66 m) with values ranging from 167 to 226 mBq/cm2 in the 0-4 cm sections, decreasing to less 20 mBq/cm3 from 10-30 cm (Fig. 2). These data indicate high sediment accumulation rates (0.40 cm/yr in average). The Pb-210 data collaborated it.

The Chernobyl accident is recorded by high Cs-=137 values (226 mBq/g) and Cs-134 presence at level 2-3 cm below surface at sediments in the core R-796-3. Cs-137 peaks (144 mBq/g) at level 2-4 cm in the core R-807-3 is also connected with it. The sediment accumulation rates in the core sites may be 0.43 and 0.57 cm/yr respectively.

Some not great peaks observed below the top layer in these cores. They are possibly the remnants of major fallout's from bomb testing beginning from 1950 and reaching their peak at 1962-63.

The mentioned remnants were apparently recorded in the upper section of sediment cores from the Kerch and Caucasian continental slope (St. R-801-1, R-803-1).

Some similarities were revealed with the results of earlier studies [1,2,3,5,7,8]

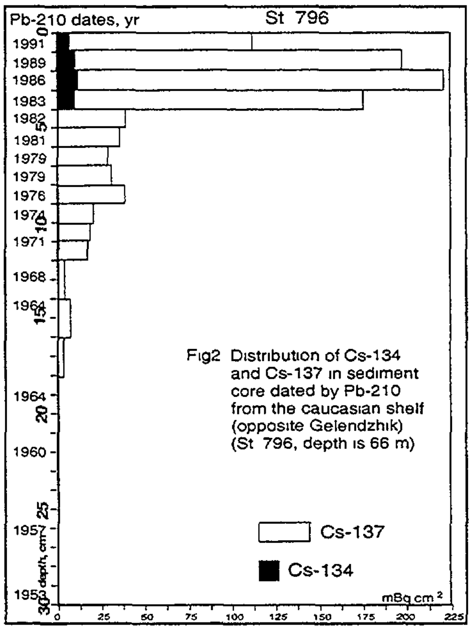

Fig2 Distribution of Cs-134 and Cs-137 in sediment core dated by Pb-210 from the caucasian shelf (opposite Gelendzhik) (St 796, depth is 66 m)

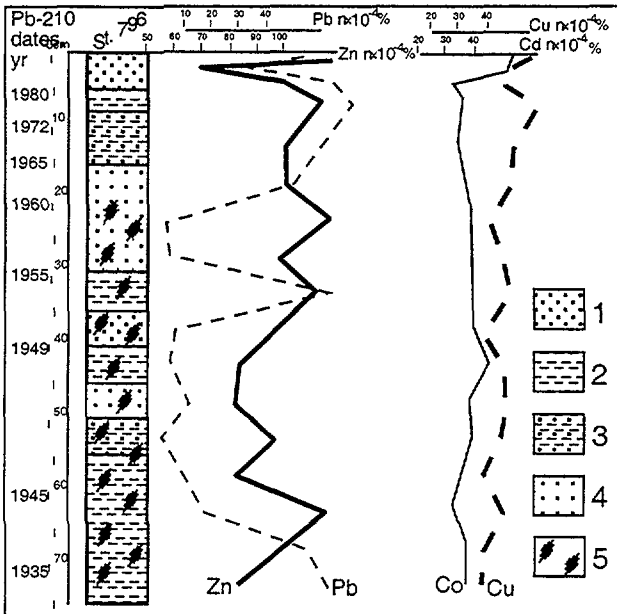

Fig3 Litology and heavy metals distribution in sediment from the caucasian shelf (St. 796, depth's 66
1-sand; 2-mud; 3-sandy mud; 4-selti sand, 5-lenses of

Heavy metals. In the core R-796 sediments are enriched in Zn, Cd, Pb in the interval where Cs-137 is detected and in the section 65-75 cm (1931-1942 yr). Upper section of deep-sea sediments (R-801, R-803) is characterised by high content of Cu and Zn. The metals trace industrial era and anthropogenic pollution of the basin.

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XA9952069

IAEA-SM-354/216P

DYNAMICS OF DISTRIBUTION COEFFICIENTS IN ESTUARINE SYSTEMS

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Selected freshwater sediments have been subjected to fresh water solutions containing ^{60}Co and ^{236}Pu. During the equilibration time, subsamples of the water phase were collected to examine the dynamics of the transfer of the radionuclides from water to sediments. After a sufficient equilibrium time, the sediments were transferred to an artificial sea water solution (salinity of 35‰). Then further subsamples were collected to study the dynamics of leaching of radionuclides from the sediments.

From the changes of concentrations of radionuclides in the water phase, time dependent distribution coefficients (K_ds) have been calculated. In addition, the contaminated sediments have been subjected to sequential extractions. The results from these experiments will be utilised to improve transport models as static K_d values are replaced by dynamic functions.

Previous studies have shown that contaminated sediments that are transferred from a fresh water (high K_d) to a marine system (low K_d) may release the contaminants (Fig. 1). [1] observed a K_d decreases of two orders of magnitude for ^{90}Sr and ^{137}Cs. In the present study, the scope is extended to other radionuclides (e.g. Pu-isotopes and ^{60}Co) and attempts are made to measure the kinetics of leaching after fresh water sediments have been transferred to high salinity water.

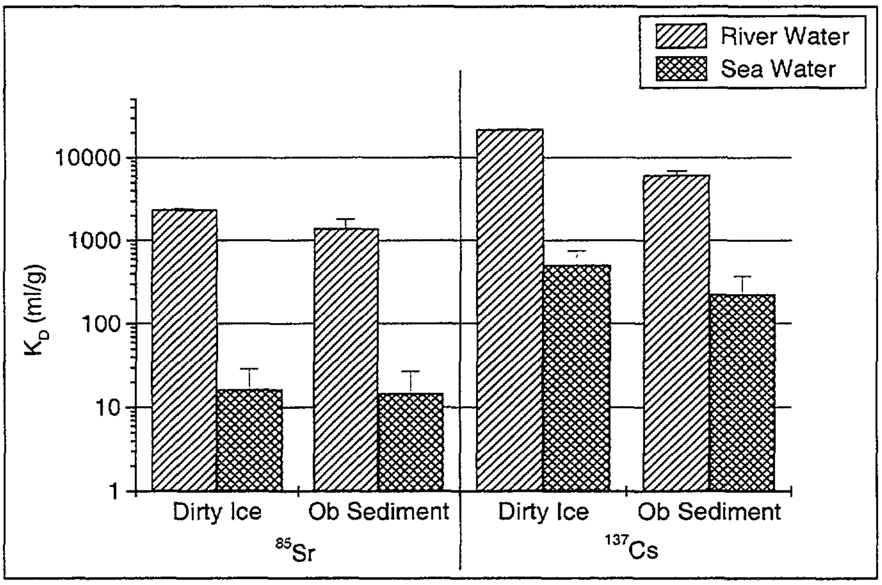

FIG. 1. Changes in K_d on transfer of two types of contaminated sediments from river water to sea water.

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IAEA-SM-354/221P

TRACE METALS IN MEDITERRANEAN MUSSEL *MYTILUS GALLOPROVINCIALIS* (L.1758) AND IN SURFICIAL SEDIMENTS FROM URLA-ÝSKELE/ TURKEY

XA9952070

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Accumulation of Pb, Cd, Cu, Zn by the Mediterranean Mussel *Mytilus galloprovincialis* and bottom sediment samples were studied monthly at Aquaculture site of Urla-Ýskele (Ýzmir Bay-Turkey). All metals showed a significant seasonal variations. The observed pattern was primarily related to the biological cycle of the mussel and only secondarily to environmental parameters. The order of enhanced metal concentrations found in mussels was Zn>Cu>Pb>Cd whereas in the sediment the order was different, i.e. Zn>Pb>Cu>Cd. In this work, the all over the metal concentrations in mussels and sediment samples from Urla-Ýskele are similar to those reported for other Mediterranean regions. The soft tissues of the mussels which still contain concentrations lie just within the range given by WHO.

In marine ecosystem, heavy metals occur in the water mass, suspended particles, sediment and biota. The use of biological indicators to monitor environmental contamination by trace metals has many advantages over the measurement of metals in water samples, since their content of pollutants harmful to marine life and it represents a time integrated image of the bioavailability of a pollutant which is not affected by short term fluctuations in sea water [1]. Trace elements, when discharged to the marine environment, will be transported by prevailing currents and removed by either physical, chemical or biological processes. Through absorption, ion exchange and complexing of chelation, trace elements are filtered by marine bivalves and picked up by particulate organic matter and settle on the bottom. So marine bivalves and their environment, i.e. bottom sediments are known to accumulate high levels of metals, and are commonly used in monitoring studies.

The aim of this research was to investigate the present status of the distribution of heavy metals (Pb, Cd, Cu, Zn) in economically important bivalve and their environment, i.e. bottom sediments from Aquaculture site of Urla-Ýskele-Ýzmir/ Turkey.

During October 1996- September 1997, samples of mussel (*Mytilus galloprovincialis*) of about 6 cm length were collected monthly from the ropes by the hand at Aquaculture site of Urla-Ýskele (Ýzmir Bay-Turkey). Immediately after collection , the shell was cleaned and the soft part samples were made from 20 individuals which had been carefully rinsed with abundant distilled water in order to eliminate sediment and other impurities. Then these samples were kept in a deep freeze (-21°C) until analysis and were prepared according to international standard methods [2]. The composite samples of mussels were weighed and digested with conc. HNO_3 : $HClO_4$ (5:1) (extra pure Merck) under reflux and filtered.

Sediments were collected monthly with a 'Orange peel' grab of capacity 4,5 l from this side at the same time. Under the fish cages then stored in plastic bags at -21°C. Each sediment sample oven dried at -60°C for 24h and then sieved using a mesh. From the dried sediment samples an aliquot of 1g. (< 160 μ) was oxidized with 10ml., conc. $HCl{:}HNO_3$ [3.1] (extra pure Merck) under reflux at 120°C for a hour and then filtered through Whatman 40 filter paper. All samples were diluted with bidistilled water and analyzed [3]. Metal samples were analyzed by Atomic Absorption Spectrophotometer using a 2380 Perkin-Elmer (AAS). Metals were determined by direct aspiration using an air acetylene flame. Intercalibration homogenate samples (MA-A-2, SP-M-1, from the IAEA, Monaco Laboratory) were used as a quality control for the analytical methodology.

In total 240 sample of mussels were analyzed. The concentrations of some heavy metals (Pb, Cd, Cu, Zn) in the soft tissues of the afore mentioned bivalve were determined. Minimum, maximum values of these metals, expressed in µg/g.wet weight in mussels, are summarized in Table I. Mean values ranged from 0.71 to 0.74 for Pb, 0.18 to 0.20 for Cd, 1.30 to 1.57 for Cu and 14.18 to 20.82 for Zn. The highest concentrations for Cd, Cu, Zn were observed in Autumn, for Pb in Spring.

Table II presents the minimum and maximum values obtained from analyzing the surficial sediments of Urla-Iskele. According to results obtained (12 samples), mean values ranged from 33.66 to 37.80 for Pb, 1.76 to 1.89 for Cd, 12.60 to 13.55 for Cu and 42.35 to 46.76 for Zn. The highest concentrations for Pb, Zn were observed in Autumn and for Cd, Cu in Winter .

TABLE I. HEAVY METAL LEVELS IN MEDITERRANEAN MUSSEL *MYTILUS GALLOPROVINCIALIS* FROM AQUACULTURE SITE OF URLA-ÝSKELE-ÝZMIR (µg/g WET WEIGHT)

Seasons		Pb	Cd	Cu	Zn
Winter'97	Min.	0,60	0,09	0,81	9,98
	Max.	0,83	0,28	1,80	20,40
Spring'97	Min.	0,68	0,11	0,94	10,21
	Max.	0,81	0,30	2,01	28,35
Summer'97	Min.	0,58	0,15	1,05	9,90
	Max.	0,85	0,21	1,98	18,46
Autumn'97	Min.	0,60	0,14	1,10	11,24
	Max.	0,84	0,26	2,04	30,41

TABLE II. HEAVY METALS CONCENTRATIONS IN SEDIMENT SAMPLES FROM AQUACULTURE SITE OF URLA- ÝSKELE- ÝZMIR (µg/g.DRY WEIGHT)

Seasons		Pb	Cd	Cu	Zn
Winter'97	Min.	31,80	1,85	12,21	30,49
	Max.	40,75	1,94	14,90	54,21
Spring'97	Min.	30,70	1,71	11,80	31,24
	Max.	39,20	1,98	13,40	55,28
Summer'97	Min.	28,79	1,68	11,75	29,94
	Max.	38,54	1,84	14,28	57,42
Autumn'97	Min.	32,21	1,74	12,01	33,48
	Max.	43,40	1,90	13,90	60,04

The Mediterranean mussel and other marine bivalves are known to accumulate high levels of metals in their tissues and are commonly used in biomonitoring studies. Bioaccumulation in marine bivalves adequately reflects the changing levels in the environment for heavy metals. The degree of their accumulation depends on their filtering activity, growth, biochemical composition, reproductive condition and metabolism. These factors are in turn affected by environmental variables such as temperature, salinity, dissolved organic matter and nutrients that influence the phytoplankton availability [4].

Previous heavy metal levels in ***M.galloprovincialis*** and surficial sediment samples are given in Table III and Table IV from different regions of Mediterreanean sea. Our results showed that metal concentrations in mussels and sediment samples from Aquaculture site of Urla-Ýskele-Ýzmir are very similar to other Mediterraenean regions subject to moderate pollution.(Table III ,IV).

The order of enhanced metal concentrations found in mussels was Zn>Cu>Pb>Cd whereas in the sediment the order was different, i.e. Zn>Pb>Cu>Cd.

All metals showed a significant seasonal variations. The observed pattern was primarily related to the biological cycle of the mussel and only secondarily to environmental parameters

The soft tissues of the mussels which still contain concentrations lie just within the range given by WHO [5]. In conclusion, it is evident that heavy metal levels in mussels can be modulated by environmental and biological factors.

TABLE III. HEAVY METAL LEVELS IN M.GALLOPROVINCIALIS, FROM ÝZMIR BAY AND DIFFERENT REGIONS OF MEDITERREANEAN (µg/g WET WEIGHT)

Locations	Pb	Cd	Cu	Zn	References
Spanish Coast	12.56	0.26	-	-	6
Inner Ýzmir Bay	1.18-1.36	0.17-1.10	1.03-6.92	10.59-279.99	7
Urla	0.18-1.35	0.19-0.42	0.33-1.42	24.15-26.12	7
Urla	1.60-3.81	0.20-0.21	2.10-9.50	20.24-26.57	8
Urla	0.60-0.86	0.41-1.12	2.20-3.10	24.10-26.60	9
Aegean Coast of Turkey	1.61	0.17	1.84	27.3	10
Scorlino-LaSpezia	0.50-16.40	-	0.38-0.40	0.19-0.58	11
Spanish Coast	0.10-50.00	0.10-2.00	1.40-3.00	20.00-60.00	12
Mediterreanean	50.00-161.00	5.00-10.60		12.00-644.00	13
Thermaikos Gulf	0.31-0.35	0.13-0.17	2.40-	-	14
Saranikos Gulf	2.09-11.02	-	154.00	-	15
	(d.w.)		2.62- 15.94(dw)		

TABLE IV. PREVIOUS HEAVY METAL LEVELS IN SEDIMENTS FROM ÝZMIR BAY AND DIFFERENT REGIONS OF MEDITERRANEAN (µg/g DRY WEIGHT)

Locations	Pb	Cd	Cu	Zn	References
Adriatic Coast	11.20-67.70	0.14-0.74	3.84-11.79	12.92-40.96	16
Lesvos Island	-	-	9.40-58.90	27.8-15.70	17
Sardinia Italy	2.52	0.12	-	13.40	18
Krka River	17.30-118.60	0.16-0.40	19.10-52.10	66.20-168.10	19
Izmir Bay	28.00-55.00	00.00-0.35	9.00-29.00	31.00-69.00	20
Urla	24.50-40.00	2.20-2.70	8.00-12.50	11.00-65.00	9
Mediterraenean	3.00-30.00	0.02-64.00	0.60-18.90	1.70-62.00	13
Aegean Sea	22.72-30.36	-	15.25-47.06	140.34-68.76	21
Lesvos Island	20.07-93.00	0.03-0.43	5.34-86.20	12.90-230.00	22

It is recommended to continue the monitoring of heavy metal concentrations in marine bivalves and their environment, i.e. bottom sediments in order to improve our understanding of their cycling in the marine environment.

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DISTRIBUTION OF POLLUTANTS IN THE RUSSIAN SECTOR OF THE BLACK SEA COASTAL ZONE

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For the latest 30-40 years the Black Sea pollution by various pollutants is observed. It is the result of economical activity intensification on the shore and of slow growth of cleaning system capacity.

In the coastal zone concentration of pollutants depends on the pollutant amount brought from the source and the process of their distribution and transport to the open sea. Within the Krasnodar region towns of Novorossiisk, Gelendzhik, Tuapse, Sochi and the ports of Novorossiisk and Tuapse are the main sources of pollutants.

On the basis of many years of research we may state that near the Krasnodar region coast there is a general longitudinal current directed from the south-east to the north-west, i.e. from Sochi towards Anapa. Velocity of this current sometimes reaches 1 m/s. This general stream is rather pronounced one during autumn-winter-spring period. In this period its mean monthly velocity is from 10 to 35 days. In summer months it is feebly marked. In different years mean monthly velocity was from 4 to 25 days. Due to a weak water circulation in summer there occur stagnant effects in the coastal zone provoked by the accumulation of pollutants in water. Sizeable areas of polluted water are formed near the sources of pollutants. Not far from the outlets of badly purified sewage waters clouds of muddy water with sharp boundaries are formed.

The research has shown also that in the shelf zone periodically 5-6 times a week there are formed anticydone eddies against a background of a general longitudinal current. When they pass the near shore zone, there occurs streams directed against a general longitudinal water shifting. Near the shore, beginning from the depth of 10-25 m, those streams become weak owing to the bottom friction. Anticyclone eddies are distinguished not only by the direction and by temperature field too. Special investigations have shown that the radius of vortexes can be 10-12 miles, i.e.- they cover the shelf and continental slope. one, streams of opposite direction are less probable. The second component is caused by anticydone eddies. Anticydone eddy is the basic mechanism of the pollutant cai-rying out of the coastal zone and of their spreading in the open sea. Basically pollutants get into the sea coastal zone from the land and ships. They are pesticides, petroleum hydrocarbons, heavy metals, organic matter, and polycyclical aromatic hydrocarbons (PAH). The largest part of them is brought to sea (or firstly to river and then to sea) by storm runoff. Smaller parts are brought to sea by wind (eolian transport). A part of pollutants gets to sea through deep sewers. It is non-cleaned wastewaters from littoral cities. On the Black Sea shore pesticides are used for spraying of vineyards, fruit gardens, tea plantations. They get to sea during the rains together with storm runoff. Early in 90's in the near shore regions about 1000 tons of pesticides were used. After 1993 their amount began to reduce And the concentration of pesticides in seawater became less one too. The main sources of pollution of natural environment by petroleum and oil-products are the following: oil fields, oil pipelines, oil-refining factories, oil storage tanks, land and water transport. Oil-products mainly get into the coastal zone from the ships, which are based in the pons of Tuapse, Novorossiisk, and Gelendzhik. That's why the port of Tuapse and Tsemess Bay are the most polluted with oil areas. In Gelendzhik Bay the highest oil-product concentration is observed at the area near the port. Oil-products can be brought to sea by storm flows as well. Mainly, it is benzine, masout, oil and other products used by transport and in private life. Organic matters, polycydic aromatic hydrocarbons (PAH), heavy metals, benzopyrene, benzoperylene, bacteria and some other pollutants are washed out from the area of littoral towns and their environs during the rain. In this period their concentration in seawater increases greatly. Thus, coli-index of seawater increases in tens. Often a high concentration of bacteria and their species composition turn to be the main reason of imposing a ban to use a beach. Heavy metals get into seawater as a result of natural processes and economical activity on the shore. Rains wash out compounds of copper, zinc, iron and other metals from littoral urban areas and arable lands. It will be presented diagrams of distribution of copper, iron, cadmium, nickel concentration in seawater As it was mentioned above, pollutants from the land get into sea coastal zone. There they are accumulated until the beginning of storm, or winds of the northern and northeastern direction. In the course of storm polluted water is carried to the open sea in the near bottom layer. When northern and northeastern winds are blowing - in surface water layer. In the open sea polluted water is captured by the stream of a general longitudinal flow directed to the northwest, or gets into anticydone eddy, which is shifting to the southeast within the coastal zone. In the last case this water is finally carried away to the open sea and dispersed. It should be noted that there is no longitudinal pollutant fluxes in the Black Sea coastal zone within the Russian section but general water transportation from the southeast to the northwest is pronounced very clearly. We can explain this phenomenon by the fact that anticyclone eddies appear periodically in the coastal zone (several times in a month). These eddies disturb a longitudinal flow and direct polluted water to the open sea, there polluted water disperses. Owing to this polluted water at the areas close to the land pollutant source is quickly and effectively replaced by clean water from the open sea. The problems concerning the increase of pollution are the urgent ones in summer during a calm water period when the current velocity reduces down the first cm/s, and in the closed bays, as well, such as the Gelendzhik Bay and the northern pan of the Tsemess Bay.

Littoral towns and the Kerch Strait are the main sources of pollution containing the Black Sea water within the Russian section. The pons of Novorossiisk and Tuapse supply a certain amount of oil-products. Since the periodical presence of the anticydone eddies, polluted water is transported to the open sea there are no longitudinal pollutant fluxes in the sea. This is why the pollutant concentration in water becomes sufficiently low one when going along the shore away from the pollutant source. The conclusion can be made that there are local centres of pollution in the Russian section of the Black Sea.

XA9952072

IAEA-SM-354/224P

EFFECT OF ENVIRONMENTAL CONDITIONS ON Cs-137 ACCUMULATIONS IN JAPANESE SEABASS (*Lateolabrax Japonicus*)

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As part of an extended marine environmental radioactivity monitoring program established by the Science and Technology Agency of Japan. The Marine Ecology Research Institute, Tokyo, has been carrying out large scale systematic measurements of some radionuclide concentrations along the coastal seas of Japan since 1984.

Samples were collected periodically to determine the radionuclide concentrations in seawater, seabed sediment and marine organisms from 15 fishing grounds near nuclear power stations and a nuclear fuel reprocessing plant .

In the results of the monitoring [1], Cs-137 concentrations in the muscles of Japanese seabass, a commercial fish in Japan, are relatively high compared with those of other species of fish. It has also been observed that the concentrations in the Japanese seabass vary widely according to the season and the location.

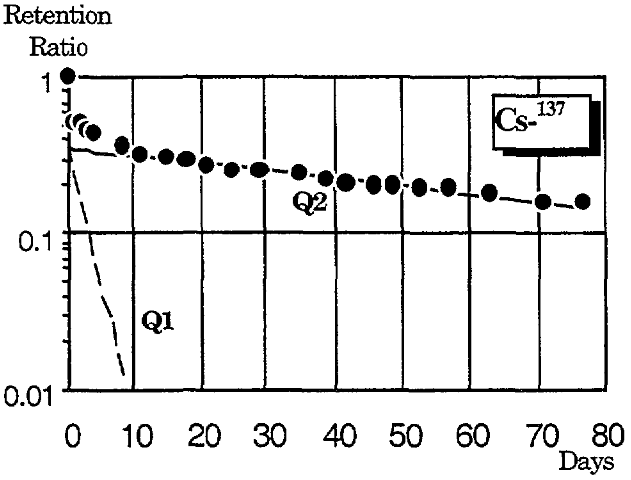

FIG. 1 The exponial model used in this study $Q(t) = K_1 \exp(-\beta_1 t) + K_2 \exp(-\beta_2 t)$

In order to inquire into the reasons for the biological behaviour of Cs-137 in the fish was examined in radioisotope tracer experiments in relation to the salinity of the environmental water as the fish migrate from freshwater to seawater in their life cycle. The accumulation and excretion of Cs-137 in the fish taken up from environmental water or from food was observed for about 80 days in seawater mixed with tap water in concentrations of 10%, 50% and 100%.

Radioactivity in the whole body and the tissues or organs of the fish was measured by using a 40· Ge (Li) detector, the data obtained were processed statistically with a program created by Shibata [2], and the biological parameters were calculated by applying an exponential model with two components (Fig.1) .

It was demonstrated that the values for the excretion rate (day-1) were smaller if reared in lower concentrations of seawater. Accordingly, the Cs-137 biological half life (Tb 1/2) of the fish kept in 10% seawater was estimated to be 2 to 2.6 times longer than that in 100% seawater. It was also recognized that the Tb 1/2 became longer with the growth of the fish (Table 1) .

TABLE I. CHANGES IN Cs-137 EXCRETION RATES (ß2) AND THE BIOLOGICAL HALF LIVES (Tb1/2:DAY) IN DIFFERENT AVERAGE BODY WEIGHTS OF FISH AND DIFFERENT SALINITIES IN AMBIENT WATER IN THE WHOLE BODY AND THE MUSCLES OF JAPANESE SEABASS (LATEOLABRAX JAPONICUS)

		fish size group	I	II	III
		average body weight	4.2(g)	16.7(g)	59.1(g)
100% seawater	whole body	(day^{-1})	0.0175	0.0110	0.0114
		Tb1/2(day)	40	63	61
	muscles	(day^{-1})	0.0136	0.0089	0.0083
		Tb1/2(day)	51	78	84
50% seawater	whole body	$_2$(day^{-1})	0.0117	0.0077	0.0065
		Tb1/2(day)	59	90	106
	muscles	(day^{-1})	0.0097	0.0066	0.0047
		Tb1/2(day)	72	105	147
10% seawater	whole body	(day^{-1})	0.0086	0.0047	0.0043
		Tb1/2(day)	80	148	159
	muscles	(day^{-1})	0.0058	0.0042	0.0032
		Tb1/2(day)	120	165	216

As a result of these experiments, the Tb 1/2 in the muscle of Japanese seabass in the case of 10% seawater at 20% was estimated to exceed 200 days. This shows that Japanese seabass that live in brackish water for a long time not only accumulate a higher concentration of Cs-137 in the muscles than those in 100% seawater but it also is more difficult to eliminate it from the muscles of the fish.

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IAEA-SM-354/225P

EFFECT OF TERRESTRIAL FLUORESCENT SUBSTANCES ON DISSOLVED ORGANIC MATTER IN THE COASTAL ENVIRONMENT

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Dissolved organic matter (DOM) plays significant rules of the chemical and physical properties for various matters in natural waters. The characteristics of DOM were changed by the effects of environmental factors such as pH, ionic strength, light and biological activities. Especially, the nature of terrestrial DOM was varied by territory of river basin (the size of the river, the nature of vegetation, etc.) [1]. In the coastal area, the terrestrial DOM is a dominant fraction of aquatic humic substances [2]. Fluorescent substances contained humic substances, which have a photoluminescence, were excited in natural waters. Specially, characteristics of riverine fluorescent substances were varied with the river basin reported by Suzuki et al. and Nagao et al. [3, 4, 5, 6]. They were carried out by three-dimensional excitation emission matrix (3-D EEM) spectroscopy. The 3-D EEM spectrum indicates important informations corresponding to the structure of fluorescent substances. In this study, the most interest is fluorescence properties of these substances in river waters corresponding to effects of territory factors. Characteristics of these substances in the river waters are investigated to understand the effects of the behavior for the radio activity elements in the coastal environment by 3-D EEM spectroscopy.

River water and sediment samples were collected from the Aidu River system, Wakayama prefecture, Japan in August and November 1997 at seven sites. The river waters were filtered with Whatman GF/F glass filters. A aliquot of the river sediment was dried at 80 ¡C and the other aliquot was stored at -4 ¡C. The 3-D EEM spectra of the samples were directly measured as follows by the method reported Nagao et al. [7]. Hitachi model F-3010 fluorescence spectrophotometer equipped with 150 W ozone-free xenon lamp was employed for the determination of the 3-D EEM spectrum.

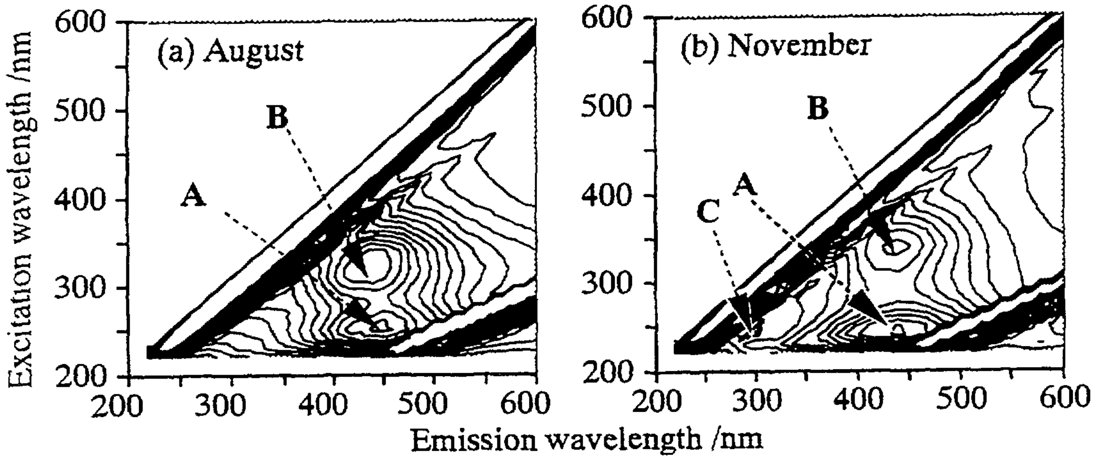

FIG.1. Three-dimensional exicitation emission matrix spectra of the river waters on August (a) and November (b). Contour intervals are 0.2 QSU for (a) and (b). the dark rows of lines running diagonally across the left and right side of the bottom panel are from Rayleigh scatters in the contour plots

The 3-D EEM spectra of river waters were characterized by two or three fluorescence peaks (Fig. 1). The peak positions in the August and November samples were excitation/emission wavelengths at 240-260/410-450 nm (Peak A), 310-340/440 nm (Peak B) and 230/300-305 nm (Peak C). In the each case of the August and November samples, the peak positions were not changed from the upper to lower streams and the tributary. Although the fluorescence peaks at the excitation of 230 nm could be detected in the November samples, the August samples did not show the fluorescence peaks. Compared among the peak positions of various humic and fulvic acids, they were good agreement with the fulvic acids. The results follow that fluorescent substances have the dominant components for the fulvic-like substances in this river system. The variations of the RFIs for the fluorescence peaks in the August and November samples showed the trend, which was increased from the upper to lower streams. These trends of the RFI variations in the other river systems have been reported by Suzuki et al. [3, 4]. Therewith, the RFIs in the November samples in wet weather were twice as high as the August samples in fine weather. The results may have been due to an increase in the water volume of the river and change of the condition of the water flux. A source of fluorescent substances in the Aidu River system may be the river sediment.

A source of fluorescent substances in this river system was investigated by model experiments. The model experiments, extraction experiment of these substances from the river sediment, were carried out by two models, which was a standing and stirring extractions. These spectra of the dissolutions from the sediments were different from the results with the directly measurements of the river waters. Therewith, the significant differences of fluorophoric systems were found between the standing and the stirring samples. The results suggest fluorescent substances eluted from the river sediments are present the chemical properties corresponding to the eluted condition. The fluorescent substances in the river are considered the corresponding to the variation of the environmental factors.

If the radio activity elements are desorpted from the atmosphere and natural waters to the sediments and soils as dry and wet despots and formed particulate matters, in the case of the river waters, the behavior and characteristics of these elements will be considered below, which are influenced of characteristics of fluorescent substances and may be transported by river run-off to the ocean in a form of fluorescent-radio activity element complexes.

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IAEA-SM-354/227P

A SURVEY OF MARINE AND AQUATIC OIL SPILLS IN THE PHILIPPINES FROM 1975-1997

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The Philippines' dependence on shipping for the conveyance of people and commodities has made it the top cause of oil spill incidents in the Philippines from 1975 to 1997. Of the 116 recorded spills during this period, 70% were ship-related; 20% occurred in refineries and depots; 7% were factory-related; and only 3% were due to undetermined causes (Fig. 1).

Fig. 2 shows the yearly frequency of oil spill accidents during this period. The year 1978 experienced the most number of accidents with a total of 5 million liters of different types of spilled oil (Fig. 3). The year 1986 had only six oil spill incidents but the volume of spilt oil reached 3.3 million liters. Hardest hit was Negros Occidental with 2.2 million liters of bunker oil emptying into the marine environment. This was the worst recorded oil spill in the country's history.

Fig. 4 shows the ecosystems affected by oil spills from 1975 to 1997. As much as 66% occurred in the marine environment, primarily due to shipping and ship-related incidents, as mentioned earlier. In this context, heavy oil or bunker fuel figured in 40% of the total spilled oil in the given period (Fig. 5). Fuel oil follows at 18%.

Fig. 6 shows that marine oil spills are caused by three related events: sinking (36%), grounding of vessels (18%) as well as both collision and sinking of vessels (10%). Other spills occurred during the transfer of oil from ships to depots or storage tanks via pipelines.

The presence of refineries and depots in Batangas and Bataan makes these areas prone to oil spills (Fig. 7). As much as 15% and 9% of oil spills occurred in Batangas and Bataan, respectively, from 1975 to 1997. In terms of volume (Fig. 8), as much as 2.8 million liters were spilled in Bataan compared to Batangas with only 0.8 million liters. Surprisingly, Pasig River and Manila Bay had almost similar number of incidents, 6%, and 5%, respectively, and volumes of spilt oil at both 0.25 million liters in the given period. However, this does not take into account the daily-undocumented spills in small volumes because of the heavy shipping traffic in the area.

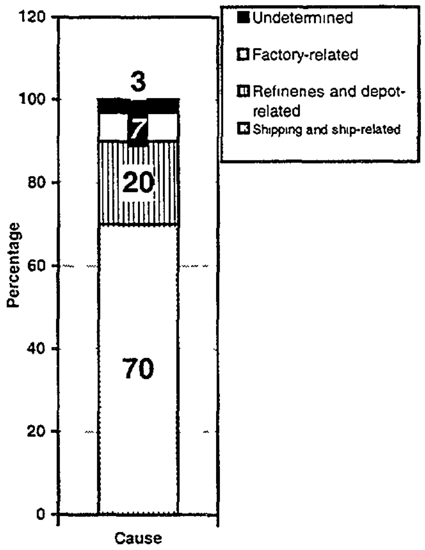


FIG. 1. General causes of oil spills from 1975 to 1997

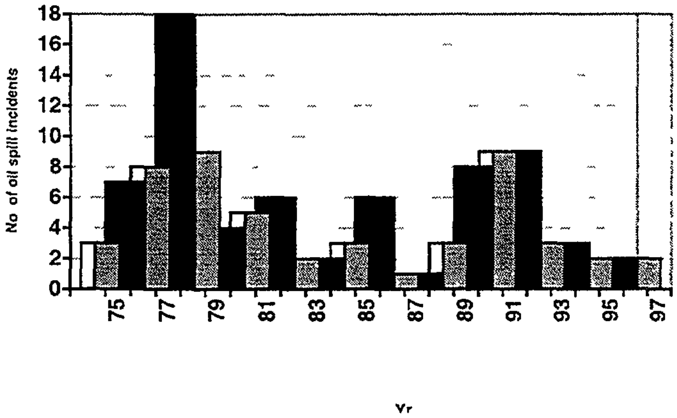
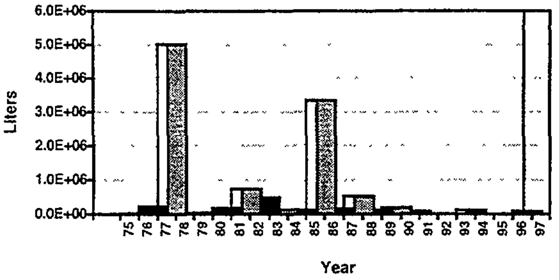


FIG. 2 . Frequency of oil spills from 1975 to 1997.



'IG. 3. Volume of oil spilled per year from 975 to 1997

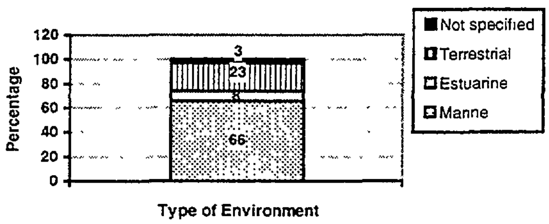
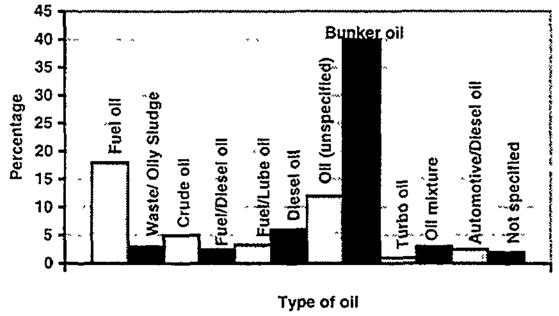


FIG. 4. Oil spill-affected environments from 1975-1997.



. 5. Types of oil spilled from 1975 to 1997.

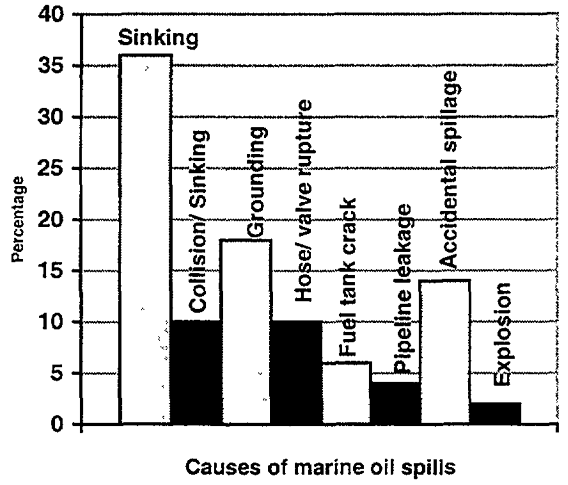
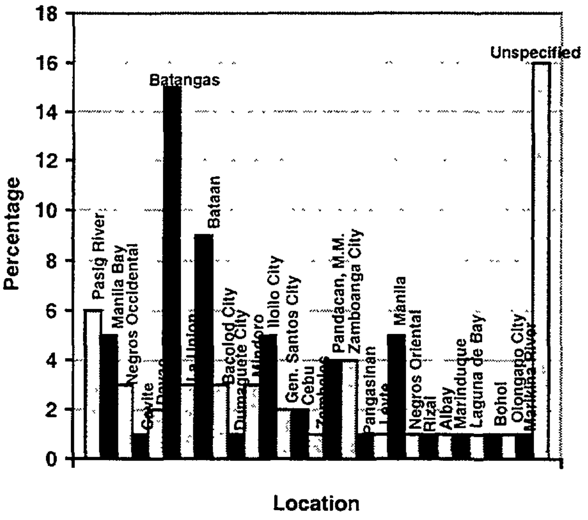


FIG. 6. Causes of marine oil spills from 1975 to 1997.



'IG. 7. Location of oil spills from 1975 to 1997.

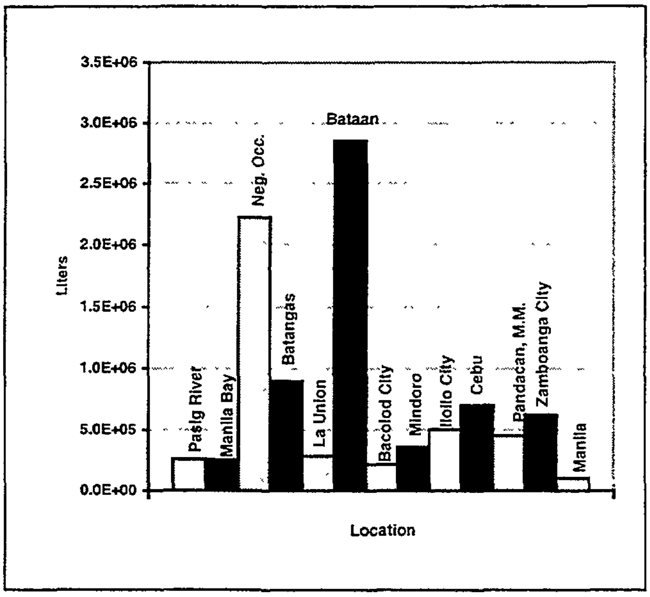


FIG. 8. Volume of oil spilled in major locations from 1975 to 1997.

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IAEA-SM-354/228P

A BIOMONITORING PROGRAM OF THE COASTAL AREA OF THE PRINCIPALITY OF MONACO

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The laboratory of ecotoxicology of the "Service de l'Environnement de Monaco" has set up a biomonitoring program in three areas of the littoral of the Principality of Monaco. This program belongs to the general monitoring program on the quality of the Environment. At a subregional level, this program is part of the programs of the tripartite agreement "RAMOGE", between the three countries France, Italy and the Principality of Monaco; the aim of this agreement being to build a pilot zone of fight against pollution in Mediterranean. At an international level, this program goes in the scope of the "MEDPOL" biomonitoring program intending to establish or to intensify programs for the continuous monitoring of marine pollution in the mediterranean zone. Our biomonitoring program consists in assessing the effects of pollutants on two marine organims (*Dicentrarchus labrax* and, *Mytilus galloprovincialis*) by using general and specific stress indices. The technique of caging is used for the animals, which are immersed at 5 to 6 m for 3 weeks. Mussels are placed in three areas and fishes are placed in two areas. At the Sporting area no special pollutant rejection is known. At the Calypso area some analyses made by the Service de l'Environnement show the presence of some pollutants. Occasionally, the Fontvieille area is submitted to the seawage of the pretreatment water station.

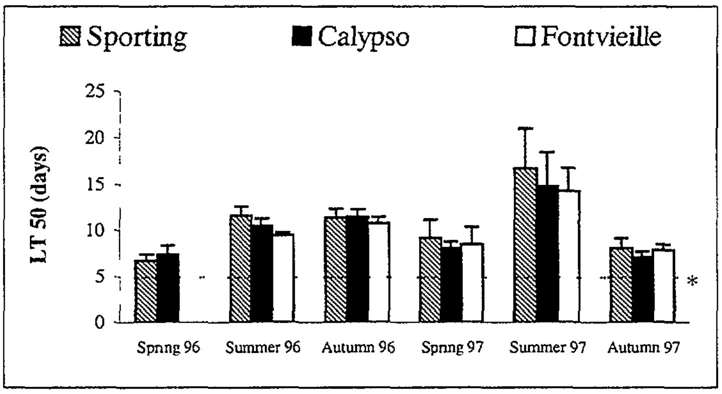

FIG 1· "Stress on stress" test, on Mytilus galloprovincialis. Values of the LT 50 (lethal time, i.e time at which 50% of the population is dead) in days ± S.E (control value)*

The values of LT 50 in control animals (i.e from a non polluted area) are of about 7 days [5]. Our results are all above this value indicating the absence of a general stress syndrom.

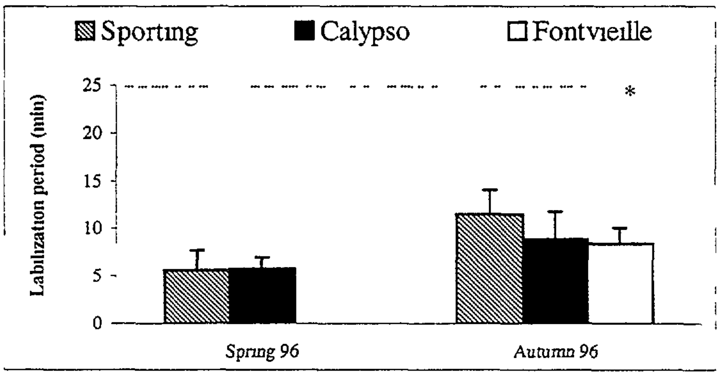

FIG 2· Lysosomal membrane stability in the digestive gland of Mytilus galloprovincialis. Values of the labilization period (LP) in min ± SE (: control value)*

The labilization period in control animals of non polluted areas is about 26 min [5]. Our values are all well below this value. This result could indicate that all the three tested areas are polluted. However since a biomarker by itself is not sufficient to give a conclusion due to all the possible biological variations, we can't conclude that these areas are polluted. Moreover the results obtained with the two other general stress indices (the neutral red retention assay (all above 1 h of retention) and the "stress on stress" test) are not in agreement with these results and are significative of a non polluted area.

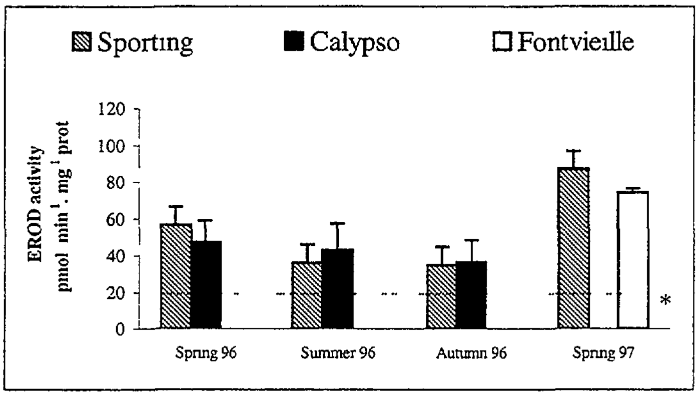

FIG 3: EROD activity in the liver of Dicentrarchus labrax (: control value).*

Since EROD activity is influenced by many biotic (species and sex) and abiotic (temperature and season) factors [1], it is hard to give a mean value of EROD activity. However during an interlaboratory comparison exercise on EROD activity in *Dicentrarchus labrax* [3], the values of control animals were all below 20 pmol. min^{-1}. mg^{-1} prot. Our results are all well above this control value indicating the presence of hydrocarbons at a level which has effect on the physiology of the fishes.

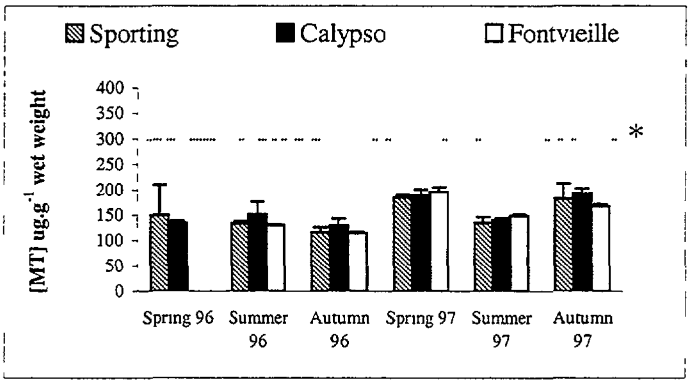

FIG. 4: Metallothioneins concentration in the digestive gland of Mytilus galloprovinciali (. control value)*

The mean value of metallothioneins concentration in the digestive gland of control mussels is about 300 µg. g^{-1} wet weight [4]. All the values found in our study are well below this control value indicating that the three areas are not polluted by metals.

Our results confirm the necessity to use a battery of biomarkers since the result of only one biomarker can lead to erroneous interpretations. The results do not show significative variations between the several geographical sites experimented in the coastal zone. The explanation which can be given to these results is that the zone is short (2 km long) and moreover the sites are in an open area. Since it's reported that biomarkers are very sensitive to seasonal parameters (see [2]) accute comparisons must be made at the same season so from now on, we'll carry on 4 sessions (at each season). When possible, we'll make the experiments both on fishes and mussels in order to have results on two important organisms of the ecosystem. As we now use the biomarkers listed above in routine, we plan to start to use new biomarkers (genotoxic effects, acetylcholinesterase, neutral lipids distribution, lipofuschins accumulation) in order to have complementary informations on the effects of pollutants at the cellular and sub-cellular levels of the organisms.

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IAEA-SM-354/230P

RADIOTRACER STUDIES ON RADIONUCLIDE AND TRACE ELEMENT CYCLING IN CORALS

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Tropical coral reef ecosystems are vulnerable to impact from land-based sources of pollution; however, information on contaminant cycling in such ecosystems is scant compared to that for temperate latitudes [1,2]. Corals are potentially useful bioindicator organisms to monitor historical trends in heavy metal and radionudide contamination [2-4] as well as paleo-oceanographic changes [5,6]. Both these uses require baseline information on the kinetic behaviour of metals and radionudides in corals.

Microcosm experiments were designed in which microcolonies of three coral species were exposed to gamma-emitting radiotracers of trace metals and radionudides (^{110}Am, ^{109}Cd .^{57}Co-cyanocobalamin, ^{110}Ag, ^{134}Cs, ^{65}Zn, ^{60}Co, ^{75}Se, ^{85}Sr, ^{133}Ba, ^{54}Mn) to determine uptake and loss as well as distribution in tissue, skeleton and zooxanthellae. Following a seven day exposure in seawater, the degree of uptake (CF = concentration factor) for a given element was highly dependent on species. The highest CF_s in whole colonies were found for ^{100m}Ag (82-172), ^{57}Co (68-124) and ^{65}Zn, (41-52); the lowest CF_s were noted for the soluble radionudides Cs (1-2) and ~~Sr (2-9). Low CF_s were recorded in skeleton and increased by roughly an order of magnitude between skeleton, tissue and zooxanthellae. ^{241}Am is readily taken up by dead skeleton (CF=31-49), whereas in living corals it is preferentially accumulated by the tissue (CF=51-120) which acts as a partial barrier against contamination of the internal skeleton (CF= 6-10). The chemical species of the element can also affect uptake by corals, as evidenced by the order of magnitude greater bioaccumulation of organic cobalt compared to the inorganic form in tissues. Once accumulated, some of the elements tested (e.g. Cd, Co) are strongly retained with biological half-lives as long as several months.

Symbiotic zooxanthellae in the corals accumulated several elements to the same degree as free-living phytoplankton (CF_s as high as 10~ for Mn and Se) and likely play a major role in metal metabolism in corals. Furthermore, these flagellates accumulated Sr (CF=3x10~) to a much greater degree than do most marine phytoplankton (CF-3) which suggests that zooxanthellae are important vectors in the deposition of Sr into the aragonite skeleton of their hosts.

These radiotracer experiments have clearly demonstrated that corals show unique responses to trace element and radionudide bioavailability. Corals take up metals and radionudides from the dissolved phase and may serve as good bioindicators for many of these elements in the environment. Accumulation and retention times vary greatly depending upon the element and the coral species. Tissue from the three species tested shows a greater affinity for most of the elements than skeleton, and symbiotic zooxanthellae may be responsible for the metabolic transfer of elements like Sr to the skeleton. Based on these findings, it is concluded that tissue and skeleton of living coral colonies as well as dead reef structure (skeleton) can serve as excellent bioindicators of anthropogenic impact and natural oscillations of radionudides and traLe elements in tropical ecosystems.

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INFLUENCE OF FOOD QUALITY ON THE ASSIMILATION, RETENTION AND DISTRIBUTION OF SELECTED TRACE ELEMENTS AND RADIONUCLIDES IN THE MEDITERRANEAN CRAB *Pachygrapsus marmolatus*

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Crabs are often used as benthic bioindicators of contaminants. A number of studies have examined the uptake and retention of radionuclides and metals from food and from water, but very few have examined the effects of different food types on assimilation, retention and distribution of these elements in benthic crustaceans. Here we present the results of radiotracer experiments which aimed to test the influence of food type on the assimilation and retention of five key trace elements and a transuranic radionuclide in a common species of crab.

Carrier-free or high specific activity radiotracer solutions of ^{109}Cd, ^{65}Zn, ^{110m}Ag, ^{60}Co, ^{75}Se and ^{241}Am were used in a mixture to label mussels (*Mytilus edulis*) for six days in sea water containing a suspension of phytoplankton cells (*Isochrysis galbana*). In addition, worms (*Nereis diversicolor*) were directly labeled from water with these same radioisotopes for six days.

Two sets of crabs (Pachygrapsus marmolatus) were fed *ad libitum* for a few minutes with prelabelled mussel soft parts or worms. Crabs fed radiolabeled mussel soft parts or worms were then dissected after 55 or 42 days of loss, respectively. Subsequent whole body radioanalysis showed that the assimilation efficiencies, biological half-lives for retention, and fecal excretion were different for the six radioisotopes in the two crab sets (Table I).

TABLE I. BIOLOGICAL HALF-LIFE (DAYS) AND ASSIMILATION EFFICIENCY (%) FOR RADIONUCLIDES AND ELEMENTS IN CRABS FED EITHER LABELED MUSSEL SOFT PARTS OR WORMS

Isotopes	Mussel food (d)*	Worm food (d)*	Mussel food %	Worm food %
^{241}Am	30±7	72±11	53±5	36±1
^{109}Cd	219±140	72±11	41±3	63±2
^{75}Se	288±28	44±10	44±3	68±5
^{110m}Ag	1232 or ∞	2458 or ∞	71±2	86±2
^{65}Zn	75±11	62±11	57±2	86±4
^{60}Co	95±29	48±9	45±2	68±5

* Numbers in bold indicate no significant difference was found between food treatments ($P<0.05$)

^{110m}Ag displayed the longest biological half-life (1232 d for mussel food and 2458 d for worm food) in the crabs labeled with the two foods. In contrast ^{241}Am was lost relatively rapidly with a biological half-life ranging from 30 to 72 days. It is also noteworthy that ^{75}Se ingested with worms was excreted much more rapidly ($Tb_{1/2}=44$ days) than when the isotope was incorporated by ingestion of labeled mussels ($Tb_{1/2}=288$ days). The data in Table 1 show that excretion of ^{109}Cd and ^{110m}Ag following ingestion of the two food treatments were not significantly different at $P<0.05$.

Data on assimilation show that except in the case of ^{241}Am, a higher percentage of the element was assimilated from food when the isotope was ingested with worms. ^{110m}Ag and ^{65}Zn displayed the highest degree of assimilation (86%) and ^{241}Am the lowest (36%) when labeled worms were ingested. In the case of the ingestion of labeled mussels, ^{110m}Ag and ^{65}Zn were also assimilated to the greatest degree; however, ^{241}Am was retained much more readily (53%) than either ^{109}Cd, ^{75}Se or ^{60}Co.

Radioisotope distributions in organs and tissues of crabs fed with mussels or worms were not significantly different. In both cases, ^{65}Zn, ^{75}Se, ^{60}Co, ^{110m}Ag were absorbed across the intestinal barrier and concentrated in crab muscle. Hepatopancreas displayed the highest radioisotope concentrations for the two groups. ^{110m}Ag, ^{75}Se and ^{65}Zn showed the greatest affinities for the exoskeleton, and ^{110m}Ag was the most reactive element with all the organs in the two groups of crabs.

The amounts of radiotracer excreted with the feces were element and food-type dependent (Table II). The data in Table 2 show that except in the case of ^{60}Co, the percentage of elements lost via fecal excretion varied greatly depending upon the food type. In general the results indicate that the radioisotopes ingested with labeled mussel soft parts are retained to a greater degree in crabs than when radionuclides are incorporated after ingesting labeled worms.

TABLE II. PERCENTAGE OF WHOLE BODY RADIOACTIVITY IN CRABS LOST VIA FECAL EXCRETION, AND THE HALF-TIME (DAYS) FOR RELEASE OF THESE RADIOTRACERS FROM FRESHLY EXCRETED FECAL PELLETS

Isotopes	**Mussel food** %	**Worm food** %	**Mussel food** (d)	**Worm food** (d)
^{241}**Am**	22	48	16±1	68±18
^{109}**Cd**	18	23	10±2	11±1
^{75}**Se**	5	11	13±2	14±2
^{110m}**Ag**	2	9	9±1	9±2
^{65}**Zn**	13	41	8±1	14±1
^{60}**Co**	17	18	13±2	22±2

Once the fecal pellets are excreted, the radiotracers were lost from the feces with half-times ranging from 8 (^{65}Zn) to 68 days (^{241}Am). With the exception of ^{241}Am in pellets produced from labeled worms, each radiotracer was lost at nearly the same rate from the fecal pellets produced from either worm or mussel food (Table 2).

We conclude from these experiments that biological half-lives, assimilation efficiencies and fecal excretion of these elements in crabs are strongly dependent on the quality of the food. Preliminary results show that the subcellular isotopic distributions in the mussel soft parts and the worm are different, however there does not appear to be a direct correlation between these subcellular distributions and the isotope assimilation efficiencies by crabs. Different isotope ligands in food or associations with subcellular fractions could influence their assimilation and retention in crabs.

HAZARDOUS CHEMICALS IN MARINE MAMMALS FROM THE WESTERN NORTH PACIFIC

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Marine mammals have long-term life and occupy the highest ecological niche in the marine ecosystem. Thus, higher concentration of hazardous chemicals are expected in marine mamals. In the present study, we review contamination of organochlorine compounds (DDTs, PCBs, HCHs, etc.), heavy metals (Hg, Cd. Pb, etc.) and butyltin (TBT, DBT and MBT) in marine mammals collected from the western North Pacific, and discuss the worldwide contamination of these chemicals.

As organochlorine compounds were liposoluble, more than 90% of the total burden in whole body was accumulated in blubber of the animals. Concentration of organochlorine compounds in the striped dolphin was about one million times as much as that in surface waters. Organochlorine compounds of adult males were higher than those of adult females, which eliminated these chemicals through lactation and parturition. Elimination rate of DDTs, PCBs and HCHs in adult females of the striped dolphin were estimated to be 91%, 88% and 72% in lactation and 4.2%, 3.8% and 6.3% in parturition, respectively. Higher concentration of DDTs was found in the animals from the tropical waters, and could be attributed to the current usage of DDT in the tropics and less movable nature of this compound via long-range atomospheric transport. On the other hand, higher concentration of HCHs was found in the animals from cold and temperate waters. This phenomenon might be reflective of atmospheric transport of HCHs from the tropical source to the northern sink. A similar pattern was also observed in PCBs, probably indicating the ongoing discharge of this compound from mid-latitude as well as that in tropical region. Concentrations of DDE and testosterone in adult male Dall's porpoises showed negative relationship, suggesting that higher DDE level could cause an imbalance of sex hormones and subsequent reproductive abnormalities in wild.

Concentrations of Fe, Mn, Cu and Hg showed the highest in liver, while those of Zn and Ni, Pb, and Cd were the highest in skin, bone and kidney, respectively. A positive correlation of metals with age was found in muscular Fe, Pb, Ni, Cd and Hg levels, in hepatic Pb, Ni, Cd and Hg levels, and in renal Hg level, while in hepatic Mn, Zn and Cu levels and renal Mn and Cu levels a negative correlation with age was found. Concentrations of Hg and Cd in the striped dolphin from Japanese waters were one million times as much as that in surface waters as well those of organochlorine compounds. In the striped dolphin, 50-70% of T-Hg and 80-90% of Me-Hg in whole body were accumulated in muscle. In the young animals of 9 years or less, Me-Hg occupied 70-100% of T-Hg, while in the older animals the ratio of Me-Hg to T-Hg decreased up to 20% with age. Concentration of Hg in fetus was very low. Transplacental transfer of Hg from the mother to her fetus was estimated at about 1%. Most (96%) of Hg in milk was composed of Me-Hg. Higher correlation coefficient (more than 0.9) was found between Hg and Se concentration in spleen, muscle and liver, suggesting that Se has a protective effect against the toxic action of Hg. Relationship between concentrations of Cd in liver and kidney was almost linear until 20 ppm in liver, where Cd level in kidney remained stationary while Cd level in liver continued to increase. This suggests that Cd concentration exceeding 20 ppm in liver might suffer disease for marine mammals such as kidney failure syndrome for humans.

Butyltin compounds (BTs) including tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT). Butyltin concentrations in liver were determined in the marine mammals and showed higher level in the animals inhabiting coastal waters than those inhabiting pelagic waters. Higher concentration of BTs was found in the animals from the waters of developed countries compared with those from developing ones. More serious BTs contamination was found in the waters of the developed countries compared with developing ones at present. The estimated concentration ratio of BTs in liver of killer whale fetus to its mother was relatively low (0.015), indicative that transplacental transfer of BTs from the mother to her fetus was a deal less. Among the BT breakdown products, DBT was predominant in most of the liver samples analyzed, followed by TBT and MBT.

At present human beings face severe global environmental problem of marine pollution, we need to study systematically on monitoring marine pollution of these hazardous chemicals. We propose the establishment of an international research network for marine pollution and an international specimen bank for marine specimens.

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A SURVEY OF HEAVY METALS IN MUSSELS (MONACO, 1989 - 1996)

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The pollution by heavy metals of the marine environment in Monaco was estimated by analysing mussels which naturally grow on the open-sea side of the main dam of the new harbour of Fontvieille (1). Sampling took place ten times between November 1989 and May 1996.

Soft tissues of mussels were removed from the animals on the day of sampling and were kept frozen at - 30°C until the analysis. Then, they were wet-ashed by nitric acid and hydrogen peroxide. Solutions of tissues were analysed by atomic absorption spectrometry using the graphite furnace technique and Zeeman background correction for Cu, Cd and Pb. Mercury was determined by the cold-vapour technique using stannous chloride as a reducing agent. The quality of results was checked by participating in IAEA/MEDPOL intercomparisons.

The analysed mussels always had a minimum size of 2.0 cm. For each sampling, the collected mussels were divided in three groups according to their size (small, medium and big size). Animals belonging to the same group of size were pooled and their soft tissues constituted a subsample for subsequent analysis. This procedure was applied in order to determine the effect of the size of mussels on their heavy metal concentrations. It was not possible, however, to keep constant the size limits for each sampling since the population of mussels on the dam naturally grew during the survey period. Collected samples of this population were essentially constituted of small size (2-3 cm) mussels in 1989 and of big size (till 6 cm) mussels in 1996.

For each sampling, the highest concentration of copper was found in small size mussels while the smallest concentration was found in big size mussels. In the case of cadmium, the effect of the animal size on the concentration was not systematic. The smallest concentrations of lead were found in the group of big size mussels and, like copper, lead concentration has a general tendency to decrease when the size of the analysed animals increases. Mercury concentrations present two peaks (in November 1991 and February 1994) and an effect of the animal size on the concentration is only visible for these peaks (the mercury concentration tends to decrease when the animal size increases). Similar effects of the influence of the size of mussels on their heavy metal concentrations were reported by other authors (2,3).

A significant correlation between metal concentrations was only found for copper and lead ($r = 0.638$, $p < 0.001$). An inverse relationship between metal concentration and animal size is significant in the case of copper ($r = -0.697$, $p < 0.001$) and lead ($r = -0.800$, $p < 0.001$).

An inverse relationship between metal concentration and sampling date is also significant in the case of lead ($r = -0.473$, $p < 0.01$). At first sight, this could indicate a decrease of the lead concentration in the surrounding sea water during the survey period. This decrease could result, for instance, from a decrease of lead concentration in gasoline (the traffic is very important in this area and can be a major source of pollution of the coastal sea water by lead).

A significant correlation, however, was also found between the average size of the mussel samples which were analysed and the sampling date ($r = 0.620$, $p < 0.001$). This is due to the above-mentioned fact that samples of collected mussels originate from a naturally growing population, the mussels collected at the end of the survey period being generally bigger than mussels collected at the beginning of this period.

As already mentioned, metal concentrations (and in particular lead concentrations) exhibit a general tendency to decrease when the animal size increases. We attribute, therefore, the inverse relationship between lead concentration and sampling date to the fact that the average size of the analysed animals increased with time, resulting in an apparent general decrease of lead concentration in mussels. If such a decrease of lead concentration in mussels really exists, it is probably very small and it is masked by the effect of the animal size on metal concentration in mussels.

Concentrations of copper, cadmium, lead and mercury in mussels collected in Monaco are of the same order of magnitude as those which were reported for other places in this area of the Mediterranean sea (4).

This work underlines the fact that the effect of the animal size should be taken into account when applying the mussel watch technique to the estimation of the state of pollution of sea water by heavy metals.

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MONTE CARLO MODELLING OF BACKGROUND CHARACTERISTICS OF HPGe DETECTORS FOR MARINE RADIOACTIVITY MEASUREMENTS

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Low-level γ-spectrometry using HPGe detectors has many applications in the environmental sciences. The reason is an excellent energy resolution that enables the analysis of several radionuclides in composite samples selectively. The radionuclide levels observed at present in the marine environment are very low, therefore a high sensitivity of spectrometric systems is required.

Though the most effective way of increasing the factor of merit of a counting system is to increase the counting efficiency and amount of sample, usually the only available way is to decrease the background of the spectrometric system. The background components of HPGe γ-spectrometers are mainly : (1) cosmic-rays (2) radioactivity of shielding materials, (3) radon and its progenies, (4) radioactivity of detector materials.

For present-day carefully designed low-level HPGe γ-spectrometers, which do not operate deep underground, the dominating background component is that induced by cosmic rays, mostly by cosmic muons. High energy cosmic rays are able to initiate a large number of complicated physical processes leading to the background induction. When one tries to quantify the background, one always has to cope with rather complicated detector-shield set-ups and physics. Obviously, analytic solutions are not possible and the only way to solve this problem is a Monte Carlo simulation.

Development of a simulation code for background induction is useful for intentional optimisation of a counting system in respect to its background characteristics. It enables to assert the background before the system has been built and also to perform systematic investigations of influence of various parameters on the background shield detector set-ups. The GEANT code [1] has been selected from the code systems facilitating simulation of passage of particles through matter as it best meets the requirements for simulations with high-energy muons. A particle random generator of cosmic muons at sea level according to the standard cosmic-muon flux was developed. Also codes for simulations of detectors placed underground with reduced muon fluxes were written using the sea-level muon generator and a muon rejection / muon momentum reduction method.

The obtained results show that the background depends most significantly on the size and lining of the shield. The most sensitive parameter of the background is the maximum value in the background continuum. Three sizes of lead shields were simulated, marked as S - small, M - medium and L - large, with cylindrical or rectangular shapes. The types of lining were descending-Z (DZ: 1mm Cd, 2 mm Cu), PBO: lead only; PC05: 0.5 cm Cu and PC10: 1.0 cm Cu. Figure 1 shows the maxima in background continua for the normal coaxial HPGe detector placed in shields marked as indicated above. C, R mean cylindrical and rectangular shields, respectively, U means 20 m.w.e. underground. The other background characteristics feature similar dependencies, except count rates in the annihilation peak which slightly decrease with increasing thickness of low-Z lining. The background characteristics of the well-type detector are similar.

The shield with a removable lining is the best choice as it can be removed in applications in which the lead X-rays do not disturb. A descending-Z lining composed of, for example, 1 mm Cd and 2 mm Cu is better than thick layers of copper only. The normal coaxial detector, which is intended for counting larger volume samples should be placed in a medium-size shield to allow also some place for the sample. It is not advisable to build the shield unnecessarily large. In this arrangement, the integral background count rate is expected to reach about 85 cpm, the count rate in the annihilation peak is estimated to be about 4400 cpd, and the maximum in the background continuum should be approximately 210 cpd/keV (at sea level). The well-type detector intended for counting of small samples inside its well should be placed into a tight shield without lining. In this case, the integral background count rate can be as small as 50 cpm, the count rate in the annihilation peak can be reduced to 1900 cpd, and the maximum in the background continuum minimised down to only about 100 cpd/keV.

The simulation of the horizontal and vertical anticompton arrangements showed that the differences between the two set-ups are negligible in the lower-energy region. Differences can be found only in the energy region above 10 MeV which is not interesting for low-level counting of environmental samples. The vertical set-up seems to be more efficient for anti-coincidence pulse rejection below about 1 MeV, but the difference is small. Therefore, the background characteristics of the horizontal and vertical set-ups are not appropriate criteria for selection of the shield orientation. Other criteria, like mechanical construction, access to the sample space, etc, should decide. The anti-coincidence pulse rejection is quite strong, at least 40 at 1500 keV and in average about 90. The maximum in the background continuum of about 200 cpd/keV is reduced to only about 1.5 cpd/keV. At this level of the anti-coincidence reduction, the other background components like contamination of shielding lead and the NaI(Tl) detectors and their photomultipliers with primordial radionuclides might dominate the background.

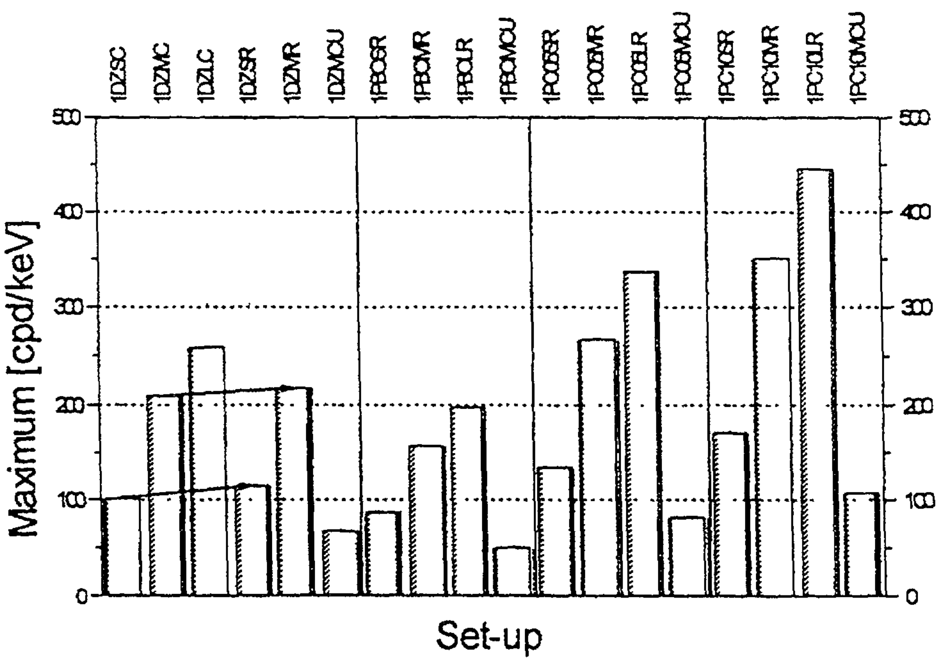

FIG. 1. Background characteristics of a HPGe detector

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TRACE ELEMENTS, PESTICIDES AND PCBs LEVELS IN SEDIMENTS OF A BAY INFLUENCED BY ANTHROPOGENIC ACTIVITIES (THERMAIKOS BAY, N.W. AEGEAN SEA)

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Thermaikos bay, in the N.W. Aegean Sea, receives about 120000 m^3/day of untreated sewage water from the city of Thessaloniki, with a population of 1200000 inhabitants. In addition an amount of about 25000 m^3/day of treated or partially treated industrial effluents is released on the northwestern coast of the bay, where the industrial zone is located, while the agricultural runoff of an area of 93542 cultivated hectares is discharged in the western part of the bay.

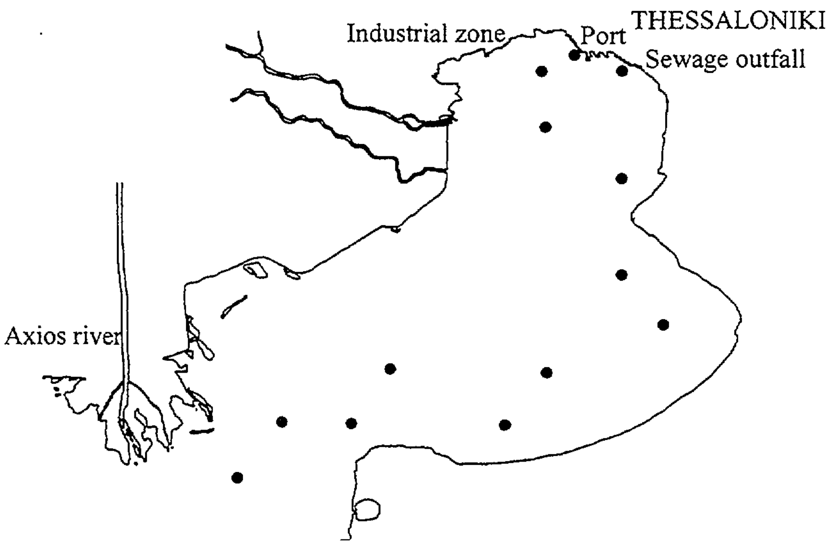

FIG. 1. The sediment sampling stations in Thermaikos bay.

Surface sediment samples recovered from the study area over a grid of 13 stations (Fig. 1) during 1995 were examined for organic carbon, Fe, Cr, Ni, Mn, Zn, Co, Cu, Pb, herbicides, DDTs and polychlorinated biphenyls (PCBs). The organic carbon was obtained according to Gaudette et al [1]. The extraction of the metals was achieved with 2N HCl and the determination of the metal content was performed on a Perkin-Elmer 305B AAS [2]. The pesticides and PCBs after extraction on a Soxhlet apparatus and clean-up on an alumina column were determined by gas chromatography on a Varian 3400 Gas Chromatograph equipped with TSD and ECD [3,4].

TABLE I. POLLUTION RATIOS OF ORGANIC CARBON AND TRACE ELEMENTS IN THE THERMAIKOS BAY

	Organic carbon	Fe	Cr	Ni	Mn	Zn	Co	Cu	Pb
Industrial zone	8.25	1.34	2.52	1.00	1.00	2.53	1.07	3.53	9.00
Port	5.96	1.13	2.14	1.08	1.02	2.73	1.00	3.41	6.00
Sewage outfall	7.45	1.18	1.61	1.17	1.00	3.01	1.07	3.06	4.50
Axios river	2.13	1.55	1.54	1.83	2.93	1.92	1.14	1.88	3.65

Organic carbon contents ranged between 0.47% and 3.30 %, Fe 1.94-3.00 %, Cr 121-305 ppm, Ni 60-120 ppm, Mn 460-1350 ppm, Zn 73-220 ppm, Co 14-20 ppm, Cu 17-60 ppm and Pb 20-180 ppm. The pollution ratios in the four sources of pollution i.e., the industrial area, the port, the sewage outfall and the Axios river are shown in Table 1. Total PCBs concentrations (the sum of 7 congeners) varied between 0.8 and 88.2 ng/g, while total DDTs (the sum of DDT and its metabolites DDE and DDD) exhibited lower values and their concentrations ranged from 1.5 to 22.8 ng/g. Atrazine, simazine and alachlor were the main herbicides detected in the area. Their concentration levels were generally low, ranging from <0.1 to 0.8 ng/g for atrazine, and from <0.1 to 0.3 ng/g for simazine and alachlor. The pollution ratios are presented in Table 2.

TABLE II. POLLUTION RATIOS OF PCBS, DDTS AND HERBICIDES IN THE THERMAIKOS BAY

			Herbicides		
	PCBs	DDTs	Atrazine	Simazine	Alachlor
Industrial zone	8.62	6.07	-	-	-
Port	110.25	15.20	1.00	-	1.00
Sewage outfall	30.62	7.87	-	-	1.00
Axios river	4.25	1.4	8.00	3.00	3.00

Organic carbon and the metals Pb, Cu, Zn and Cr show a clear influence from the three "anthropogenic" pollution sources, namely the industrial zone, the port and the sewage outfall, with pollution ratios ranging from 1.61 to 9.00. On the contrary, the metals Fe, Ni, Mn and Co show pollution ratios around 1.00 in the three aforementioned pollution sources and higher pollution ratios in the Axios river, suggesting their mostly natural origin. PCBs present extremely high pollution ratios at the stations close to the port (110.25) and the sewage outfall (30.62), indicating that the anthropogenic activities in the city of Thessaloniki are very important sources for these pollutants. DDTs also present the higher pollution ratios in the same pollution sources, while for the herbicides, chemical species being used exclusively for agricultural purposes, it is clear that the land drainage through the rivers plays the most important role for their transport in the marine environment.

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UPTAKE AND LOSS OF HEAVY METALS AND RADIONUCLIDES IN THE COMMON NE ATLANTIC STARFISH *ASTERIAS RUBENS:* SEAWATER AND FOOD EXPOSURES

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The common asteroid *Asterias rubens* is a widely distributed species in the NE Atlantic, both geographically and bathymetrically (from 0 to 650 m depth). It is a top-predator species, feeding mainly on filter-feeders, and it forms stable, sedentary and abundant populations. It has also been shown to efficiently accumulate metals [1,2,3]. These facts suggest that it could constitute a valuable bioindicator of metal contamination. However, few studies have investigated bioaccumulation in *A. rubens* using realistic metal concentrations. Here, biokinetics were investigated using radiotracer techniques in order to (1) study contaminant concentrations representative of those normally encountered in the marine environment and (2) further assess the value of *A. rubens* as a sentinel organism for identifying and monitoring metal contamination in the environment.

Seven radiotracers were selected: ^{54}Mn, ^{57}Co, ^{65}Zn, ^{110m}Ag, ^{109}Cd, ^{134}Cs, ^{241}Am. Bioaccumulation was followed in asteroids of the same size class (radius length: 4 ± 0.5 cm) exposed for 32d via sea water or for 48h through the food (mussels *Mytilus galloprovincialis* previously exposed to the tracers for 35d). Depuration was followed by maintaining the same exposed asteroid individuals under non-contaminating conditions for 63 and 70d, respectively.

When *A. rubens* was exposed to the tracers via sea water, only Ag and Cs displayed saturation kinetics over the duration of the experiment. These kinetics were characterized by a steady-state whole-body concentration factor (CF) of 336±10 for Ag and 4.7±0.8 for Cs. All the other elements displayed linear uptake kinetics (with whole-body CF at the end of the experiment ranging from 18±5.2 to 485±111). Bioconcentration is body-compartment dependent: Mn, Co, Zn, Cd and Am were more efficiently concentrated in the calcified body wall (CF up to 1320) whereas Ag and Cs were mainly concentrated in the non-calcified body compartments (stomachs, pyloric caeca, and gonads; CF up to 2180).

Loss kinetics varied according to the element: Ag and Cs were very rapidly eliminated (with biological half-lives -$T_{b1/2}$- of 9 and 7 d, respectively), Mn, Co and Cd showed similar $T_{b1/2}$ (22 to 27 d), and Zn and Am displayed the highest retention times with $T_{b1/2}$ of 53 and 63 d, respectively.

On a metal load basis, the major fraction (89 to 99%) of Mn, Co, Zn, Cd and Am was found in the body wall, whereas Ag and Cs were homogeneously distributed between body wall and pyloric caeca (the latter ones accounted for 35 to 45% of the total activity). Element distribution remained unchanged throughout the contamination and depuration periods.

Loss kinetics of the elements incorporated through the food (mussels) was best fitted by a single exponential equation. These losses were more efficient than following incorpoation from sea water; e.g. 90 to 100% of all investigated elements were lost after a 70d-depuration. With the exception of Cs, tracer $T_{b1/2}$ were found to be much shorter after an exposure through the food than after an exposure via sea water, indicating a less efficient retention of dietary metals.

Elements showed a time-dependent body compartment distribution. Shortly after ingestion, radiotracers were mainly (50 to 78%) found in the pyloric caeca, while 70d after feeding they were rather homogeneously distributed among all the body compartments, indicating effective translocation from the pyloric caeca (these organs are the main site of food assimilation in asteroids) to all the other body compartments of the animal.

Though food may be a significant contributor to metal contamination in *A. rubens*, sea water appears to be the predominant route for metal bioaccumulation in this starfish. The results show that *A. rubens* is an efficient bioaccumulator that would be able to preserve information concerning levels of environmental contamination by metals on a time scale of months.

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IAEA-SM-354/241P

THE FATE OF ^{137}Cs IN THE COASTAL SEAS OF JAPAN AND RESULTANT DOSE FROM INTAKE THROUGH FISHERY PRODUCTS

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The relationship between the flux of the atmospheric ^{137}Cs at the surface of the sea and the concentration in seawater was studied in order to elucidate its fate in the marine environment and to assess the radiological impacts to the human population. A simplified mathematical model was introduced to the present study assuming the first order kinetics to apply to the time course of ^{137}Cs radioactivity concentration in seawater, that is:

$$\frac{dC}{dt} = F(t) - \lambda C \qquad [1]$$

where **C** was the time-dependent function of the ^{137}Cs concentration in seawater, **F(t)** was the flux of ^{137}Cs to the sea and λ was the constant of depletion of ^{137}Cs in the sea. As far as the fallout ^{137}Cs originating from nuclear test explosions in the past is of concern, it would be difficult to give a specific function to **F(t)** in the equation above because of almost complete irregularity both in the time and scale of the events. When the initial concentration of ^{137}Cs in seawater is given as $\mathbf{C_0}$ in case of a single release, the solution of Eq (1) can be given by:

$$C = C_0 \exp(-\lambda t) \qquad [2]$$

If the deposition density of ^{137}Cs is observed at intervals of time, τ, the concentration in seawater is given as follows, when ^{137}Cs is supposed to deposit at the very beginning of the period of time, τ:

$$\begin{aligned} C &= d \cdot F_1 \cdot \exp[-\lambda(m-1)\tau] + \cdots + d \cdot F_i \cdot \exp[-\lambda(m-i)\tau] + \cdots + d \cdot F_{m-1} \cdot \exp(-\lambda\tau) + d \cdot F_m \\ &= \sum d \cdot F_i \cdot \exp[-\lambda(m-i)\tau] \qquad [3] \end{aligned}$$

where $\mathbf{F_i}$ is the deposition density at the **i-th** interval of a total of **m** times observations, **d** is the conversion factor from the deposition density to concentration in seawater with a dimension of $\mathbf{L^{-1}}$. The parameters, **d** and **λ**, relating to the oceanographic properties of the sea are expected to be provided by means of a regression analysis when the data both on the deposition density of ^{137}Cs and on its concentration in seawater are given. If a set of data above mentioned are given along with the approximate values, $\mathbf{d_1}$ and $\mathbf{\lambda_1}$ for the parameters, **d** and **λ**, the exact value of ^{137}Cs concentration in seawater can be estimated in the following formula as a result of the Taylor's expansion of the Eq [3]:

$$C_{ext} = C_{app} + (d - d_1)\left(\frac{\partial C}{\partial d}\right)_{d=d_1} + (\lambda - \lambda_1)\left(\frac{\partial C}{\partial \lambda}\right)_{\lambda=\lambda_1} \qquad [4]$$

where $\mathbf{C_{ext}}$ and $\mathbf{C_{app}}$ are the exact value, namely, the observed concentration of ^{137}Cs in seawater and the concentration obtained by calculation, respectively. Eq(4) can be regarded to be analogous to the equation expressed in the form, $\mathbf{Y=AX_1+BX_2}$, and therefore, the second approximate values, $\mathbf{d_2}$ and $\mathbf{\lambda_2}$ can be derived by an ordinary least square method. The most provable values for the parameters, **d** and **λ**, thus, can be determined when the difference between the results of the repetition of calculation becomes negligibly small.

When ^{137}Cs is released uniformly to the sea in the same manner as the worldwide fallout, the infinite time integrated concentration of radioactivity in the seawater can be given as follows:

$$\int_0^\infty C dt = \lim_{n\to\infty}[d \cdot \tau \cdot F + d \cdot \tau \cdot F \cdot \exp(-\lambda\tau) + \cdots + d \cdot \tau \cdot F \cdot \exp(-n\lambda\tau)] = \frac{d \cdot \tau \cdot F}{1-\exp(-\lambda\tau)} \qquad [5]$$

The dose commitment for the member of the public denoted by **E** and that for the whole population denoted by $\mathbf{E_g}$ affected by the release of ^{137}Cs to the sea would be provided as follows:

$$E = \Phi \sum_r I_r \cdot CF_r \cdot \int C dt, \qquad E_g = \Phi \sum_r Q_r \cdot CF_r \cdot \int C dt \qquad [6]$$

where **Φ** is the dose intake conversion factor, $\mathbf{CF_r}$ is the concentration factor of ^{137}Cs by the species of marine organism, **r**, $\mathbf{I_r}$ is the consumption rate of the organism, **r**, by an individual, and $\mathbf{Q_r}$ is the total catch quantity of the organism, **r**, in the region of the sea of concern.

The parameters involved in Eq(3) were numerically derived for three regions of the coastal sea of Japan by the regression analyses as mentioned above from a series of radioactivity survey data reported for the past thirty years since 1960. Figure 1 is a schematic expression of an example of the results obtained. It is anticipated that ^{137}Cs was retained in the coastal sea of Japan with a half-life period ranging from 5.3 to 6.8 years without a great difference between the Pacific Ocean and the Japan Sea. The integrated concentrations of ^{137}Cs in seawater were determined as 0.19, 0.17 and 0.12 mBq·a/l, respectively for the coast of Ibaraki/Fukushima, Niigata and Fukui Prefecture as a result of the deposition at a unit density (1MBq/km^2) at a time. The resultant dose commitment of the respective inhabitants would be 4.1, 3.7 and 2.6 nSv through the coastal fishery products and that of the population would correspond to 4.5, 2.4 and 0.9 man·Sv, respectively.

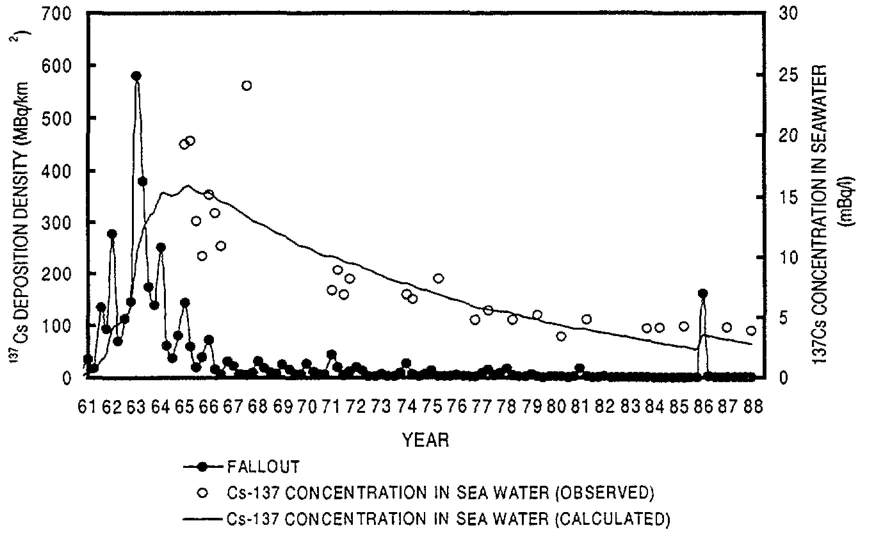

FIG.1. Course of Time of Deposition of Fallout ^{137}Cs in Ibaraki/Fukushima Prefecture and its Concentration in the Coastal Seawater

IAEA-SM-354/242P

OCCURRENCE OF CHLORINATED PESTICIDES IN MUSSELS OF GUANABARA BAY, RIO DE JANEIRO, BRAZIL

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Chlorinated pesticides are common pollutants in the aquatic environment in coastal areas and estuaries [1], [2], [3]. Guanabara Bay is a coastal area of great economical importance and leisure interest in the Brazilian Southeast Coast. It is surrounded by two cities, Rio de Janeiro and Niteroi, with a total population of about eleven million inhabitants. The Bay receives a daily discharge of chemical contaminants introduced with several tons of domestic, industrial and agricultural treated and non-treated sewage. Part of these contaminants may be incorporated by the living organisms of this ecosystem and consist of potential danger to human consumption. Present work investigates the contamination of some chlorinated pesticides in common mussels (Perna perna) [4], [5] from the Guanabara Bay. These mussels can be found in several points near the entrance of the Bay, where they either grow naturally or are cultivated by fishermen which make their living of this activity. Five collecting areas were studied and the concentrations of eight pesticides, namely HCB, γ-HCH, total DDT, DDD and DDE, Aldrin, Dieldrin and Endrin were determined. The samples were collected twice a year, during the dry (August) and rainy (December) seasons of 1996. The mussels were manually collected, wrapped in aluminium foils previously rinsed with acetone, ethanol and hexane for pesticide analysis and kept frozen until reach the laboratory. After selection, 10 (ten) mussels of similar size (4-6 cm) composed one sample for each location. The muscle tissues were separated from the valves and were cold frozen-dried, so the water content was removed without loss of volatile components. The material was ground and homogenized and kept ready for the analysis under -10^0C. A mussel sample (2g) was spiked with known amount of tetrachlorometaxilene (TCMX) and was Soxhlet extracted for 24 hours with pesticide grade hexane purified through Florisil columns. The extract was concentrated to about 10 mL in a rotary evaporator and cleaned up by vigorous shaking with 2 mL of concentrated sulfuric acid. Phase separation was achieved after 12 hours in the icebox; the upper hexane layer was removed and passed through an alumina short column deactivated with 5% water. The solution was eluted with a mixture of hexane-dichlorometane (90:10) and evaporated under nitrogen flow. From this concentrated extract an aliquot of 500μL was transferred to the automatic injector vial where 100μL-volume of $0.1\text{ng}.\mu\text{L}^{-1}$ solution of trichlorobenzene (TCB) was added as an internal standard. The recoveries calculated from the added TCMX offered a mean value of 76%. The extracts were analyzed in a gas chromatograph (Varian Star 3600 CX Model) using Ni^{63} electron-capture detection and fused silica DB-5 capillary column (J&W Scientific) of 50m x 0.25mm ID dimensions and film thickness of 0.25μm. Splitless mode injections of 1μL-volume were used for all samples. Column temperature programming started from 80^0C to 205^0C at 5^0C.min^{-1}, with an isothermal period of 15min., followed by a second step program from 205^0C to 290^0C at 2^0C.min^{-1}. The analytical conditions provided good separation for the pesticides of interest and PCB peaks (Aroclor 1254 and 1260) eventually present in the samples. The analytical method was applied to a certified sample for pesticide mussel contamination. The results obtained were kept within the confidence interval.

The results obtained for all samples are listed in Table I.

TABLE I. RESULTS

Pesticides Concentrations (ng/g)

	August					December			
collect. point	*1*	*2*	*3*	*4*	*5*	*1*	*2*	*3*	*5*
HCB	0.16	4.59	0.15	0.07	0.64	0.001	0.0002	1.66	0.90
Lindane	3.23	2.61	1.93	4.45	5.89	0.822	0.81	0.89	1.02
DDE	18.3	5.20	43.9	0.60	13.6	4.91	3.53	9.89	21.7
DDD	2.05	1.31	6.53	2.40	19.5	0.63	0.91	0.28	5.80
DDT	16.9	6.86	13.6	6.55	5.53	3.30	2.40	0.34	4.19
Aldrin	2.26	3.42	1.76	3.83	7.29	0.57	1.34	0.63	1.07
Dieldrin	2.67	2.87	14.9	4.01	5.08	2.66	1.50	2.47	0.54
Endrin	*	*	*	9.91	12.3	*	2.35	*	1.49

* = not determined

The results showed that the mussels Perna perna from Guanabara Bay are contaminated by chlorinated pesticides; however the contamination decreases drastically in the rainy season. A location where natural population of mussels is used for regular consumption was considered the less polluted one.

DDT's were the contaminants present in larger amounts and among them the DDE predominated. The smaller concentrations were found for HCB.

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CHANGES IN MARINE FISH COMMUNITY UNDER INFLUENCE OF LENINGRAD NUCLEAR POWER PLANT AND ANOTHER HUMAN ACTIVITIES IN THE WATERSHED OF KOPORSKAYA BAY (GULF OF FINLAND, BALTIC SEA).

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The long-time observations (1978-1997) in the Leningrad nuclear power plant cooling water-body (Koporskaya Bay) in the frame of the Regional Ecological Monitoring Program provided reliable data on the local fish community state.

Regular observations allow us to trace structural changes in fish community, because they follow changes on physiological and population levels in this community. 45 species of fishes and lamprey were recorded during all investigation period. However, the species diversity is very poor. Wittaker dominance-diversity curves (Fig.1) reflect degradation in the coastal fish community being under influence of the complex industrial and agricultural factors. The fish community is now dominated by only 2-3 species, especially threespined stickleback and ninespined stickleback; while the first species more abundant then the second one as far as ~10 times.

Using a number of the most frequent species in our samples (frequency > 50%), known as a community nucleus, as an indicator of natural condition of the water-body, we recognized following: in 1980 the nucleus was formed by 9 species, in 1981-1985 - 7-8 species, in 1986 - yet 6 species, in 1989-1995 - only 4-5 species, but in 1996-1997 the number dropped to 2-3 species. Thus, the trend is not very optimistic. One of the most objective information indices - Shannon-Weaver index - reflects fluctuations in the fish community of Koporskaya Bay in 1981-1997 (Fig.2).

The fish losses caused by the cooling system of NPP are significant. Most part of intrained fish is presented by young-of-year small fishes and older but weak and damaged fishes. Thus, young-of-year, 1-year old and 2-year old baltic herrings composed 98% in all number of this species in samples. There are no any fish protecting facilities at two NPP water-input canals. The fish removing system at the pump station is very imperfect, so most part of fishes perished there. That is why fish losses in the NPP water-intake facilities are comparable with commercial fish catches in the bay. Thus, NPP water-intakes promote structural changes and prevalence of fish species of low commercial value in the community.

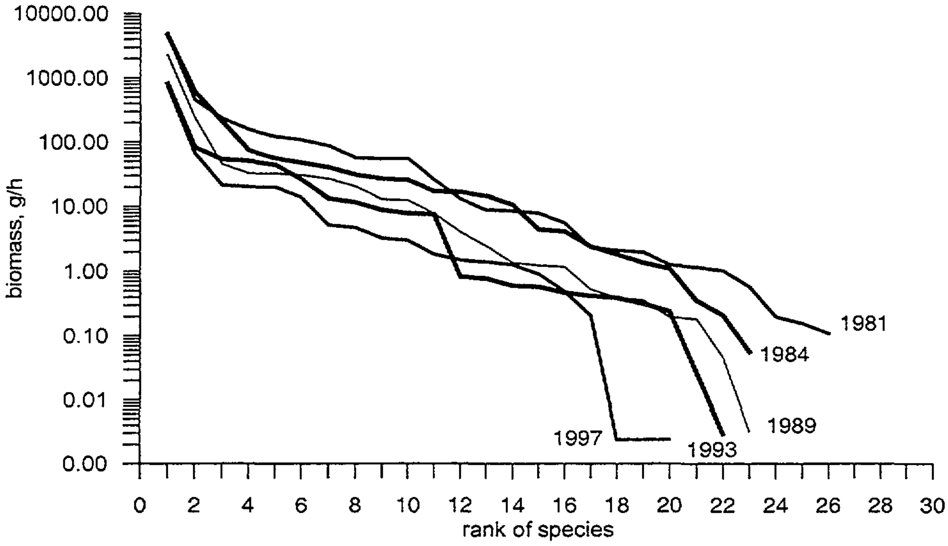

FIG. 1 Wittaker dominance-diversity curves for the fish community of NPP water-input area.

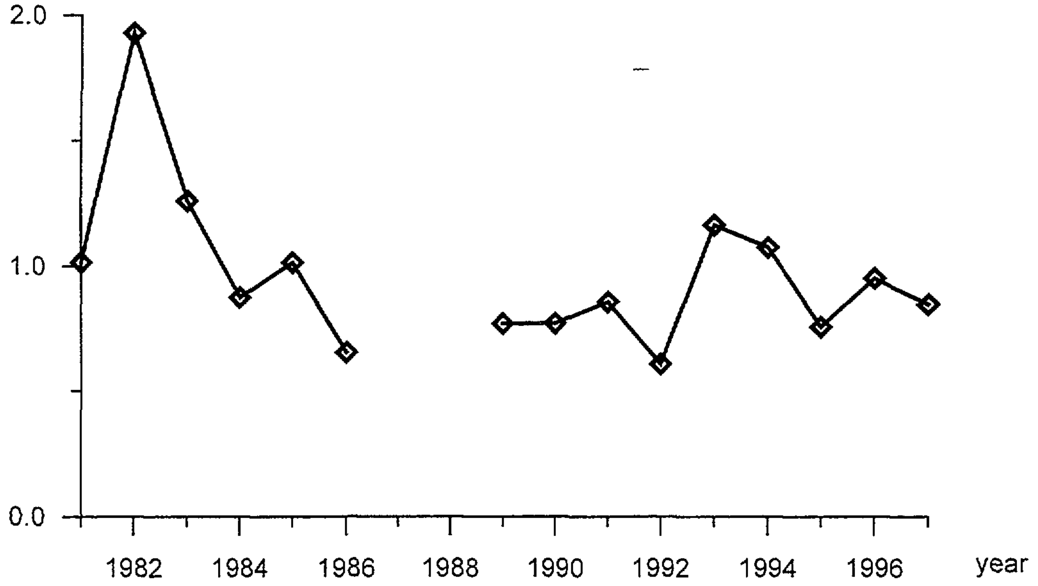

FIG. 2. Shannon-Weaver information index for the fish community of NPP water-input area.

IAEA-SM-354/248P

THE FATE OF NUTRIENTS AND PHOSPHATES IN AKROTIRI BAY, CYPRUS BASIN (EASTERN MEDITERRANEAN LEVANTINE BASIN)

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The pathways and the levels of the concentrations of nutrients resulting from the discharge of treated effluents from the Limassol Sewage Treatment Plant (SALA) and from marine fish farms in Akrotiri Bay were studied through numerical simulations of the dispersion of phosphates and nitrates. The use of a dispersion model made it possible to evaluate different courses of action regarding both, the protection of the marine ecosystem and the development of marine fish farm activities. Akrotiri Bay is a semi-open coastal sea area in the Eastern Mediterranean Levantine Basin bounded to the North and West from the south coastline of Cyprus. Nutrients inputs from the discharges of SALA result in the elevation of the background levels of nutrients and in particular those of phosphates.

The flow in the Cyprus Basin and wind forces are capable of influencing the circulation in Akrotiri Bay. The northern periphery of the mid-Mediterranean jet and the western extension of the Cyprus Basin Cyclonic Eddy contribute to the formation of a local eastward flow in spring and autumn (1996) [1]. The Lagrangian current meter measurements in the coastal zone of interest confirm a marked seasonal flow variability, eastward during winter and spring and westward during summer and autumn [2].

In order to investigate the possible long distance transport and the dispersion of nutrients in Akrotiri Bay, 2D and 3D flow and dispersion models [3] for conservative pollutants in a homogeneous water column was applied (the upper mixed layer reaches down to 30-40 m depth- much deeper than the depth where most of the fish farm units are located). In accordance with the dominant wind field, the westerly and easterly sector winds are used to force the flow model. The westerly sector winds generate in the bay an eastward current flowing along the coastline and a small scale cyclonic vortex near the western coastline. A reversal of the currents was simulated in the case of easterly sector winds. Both cases are in agreement with the observed current measurement [4].

Several numerical experiments have been performed to simulate the pathways of conservative pollutants for nitrate and phosphate loads from SALA and those due to existing and planned marine fish farms in the bay. The dispersion models used to simulate the conservative pollutant concentrations. Nitrates are utilized by phytoplankton which extrudes part of the assimilated nitrogen because of respiration and mortality rate, creating detritus, which is remineralized in nitrates. The aggregated formulation is conservative under the simplifying hypothesis that the non conservative processes of the nitrogen cycle are in dynamic balance [5]. The existing nutrient loading of the marine environment in Akrotiri Bay is 22 tonnes of Nitrogen and 4.4 tonnes of Phosphorous per year. The model simulations for dissolved nitrogen and phosphorous indicate that the SALA sea outfall and the marine aquaculture production increase these nutrients by 0.14 mmolN M-3 and 0.04 mmolP M-3. The present nutrient loading in the area, based on in-situ measurements, results in 100% and 15-30% increases of the winter background levels of phosphate, at a distance of 4 and 10 km from the SALA outfall respectively [6]. The % increase of phosphate concentrations during spring and summer periods are much higher as the background levels are practically zero.

Westward simulated dispersion of phosphates in Akrotiri Bay from existing sources.

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DISTRIBUTION OF Cs-137 AND Pu-239+240 IN MARINE SEDIMENTS FROM BRAZILIAN SOUTHERN COAST

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This paper reports the results obtained in the analysis of Cs-137 and Pu-239+240 in marine sediments as well as mean deposition historic of these radionuclides in the marine environment. Cs-137 and Pu-239+240 measurements were performed in marine sediments in order to estimate the deposition of these radionuclides, at 1976 to 1986, and to compare these measured values with those expected from global fallout. Samples were collected at the water-sediment boundary at several characteristic depths, from 15 to 180 m by the Oceanographic Institute (São Paulo University).

For Cs-137 analysis, samples were counted in a low background Ge detector (60% efficiency), using methodologies already implemented [1].

Pu-239+240 analysis consisted of sediment lixiviation (8 M nitric acid in the presence of plutonium tracer), ferric hydroxide coprecipitation, dissolution in 8 M nitric acid and addition of sodum nitrite, purification by using anionic exchange columns (Bio-Rad AG-1X8, 100-200 mesh, 8 M nitric acid medium), electrodeposition and counting by alpha spectrometry [2].

Table 1 shows the levels of Cs-137, Pu-239+240 and the Pu-239+240/Cs-137 ratios in the samples analyzed. Cs-137 levels ranged from 0.40 to 2.25 Bq.kg^{-1} and for Pu-239+240 varied from 4 to 227 mBq.kg^{-1}. The ratios ranged between 0.005 to 0.338 showing that the radionuclide deposition is related to the mobility of cesium and plutonium inside the sediment as well as its mineralogical composition. The minimum and maximum ratio values were found for sediments with the following characteristics , respectively: particle medium diameter (6.23 and 0.96 μm); sand (22.4 % and 99.4 %); silt (43% and 0.6 %); clay (35% and 0%) and carbonate (87% and 3%).

Based on the experimental radioactivity values obtained for Cs-137 and Pu-239+240, the mean deposition of these radionuclides in sediments, in different years of sampling, were calculated by taking into account the concentration of radionuclide at slide 1, dry weight and section of slide 1 [3]. Results are shown in Fig.1.

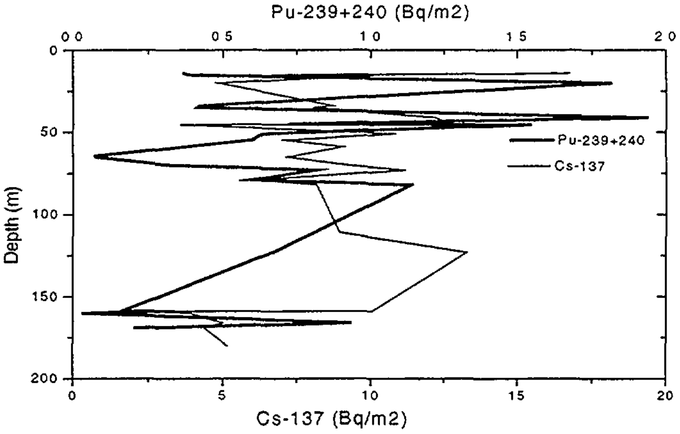


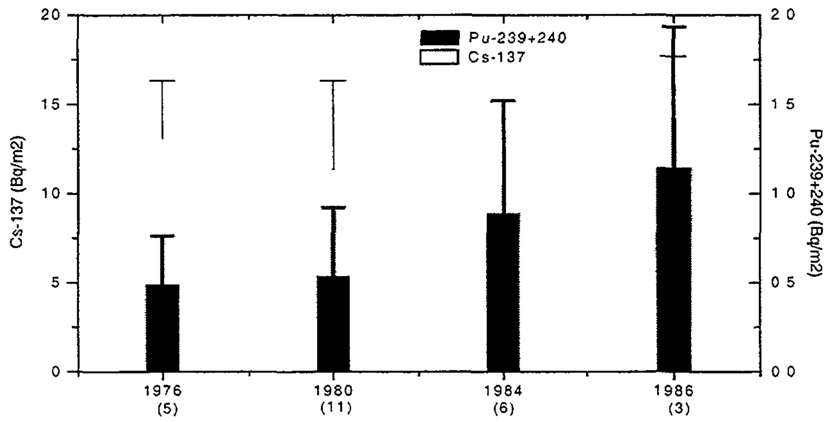
FIG.1. Mean deposition of Cs-137 and Pu-239+240 in sediments at different depths. All data were ± corrected for physical decay to 1997.

TABLE I. LEVELS OF Cs-137 AND Pu-239+240 IN SEDIMENTS

Sample	Year	Depth (m)	Latitude	Longitude	Pu-239+240 ($mBq.kg^{-1}$)	Cs-137 ($Bq.kg^{-1}$)
1862	1976	73	24°51.0'	45°52.0'	90 ± 8	2.03 ± 0.13
1865	1976	65	24°32.0'	45°58.0'	8 ± 2	1.18 ± 0.08
1878	1976	55	24°13.0'	45°40.0'	56 ± 5	1.09 ± 0.10
1879	1976	34	24°04.0'	45°44.0'	40 ± 5	1.35 ± 0.13
1885	1976	79	24°33.0'	45°18.0'	52 ± 3	0.86 ± 0.08
1809	1980	166	25°09.2'	44°56.0'	117 ± 10	1.42 ± 0.19
1812	1980	111	25°10.0'	45°24.0'	ND	1.54 ± 0.12
1815	1980	159	25°37.0'	45°13.0'	133 ± 10	1.72 ± 0.24
1825	1980	51	25°00.0'	46°36.0'	62 ± 5	1.47 ± 0.07
1831	1980	169	25°50.0'	45°32.0'	22 ± 3	0.68 ± 0.12
1832	1980	180	25°50.0'	45°53.0'	ND	0.74 ± 0.15
1834	1980	123	25°32.0'	46°20.0'	76 ± 7	1.66 ± 0.21
1835	1980	59	25°08.0'	46°48.0'	ND	1.16 ± 0.12
1839	1980	70	25°47.0'	47°09.0'	28 ± 5	1.23 ± 0.07
1842	1980	159	26°14.0'	46°32.0'	37 ± 3	0.37 ± 0.18
1852	1980	160	24°25.0'	44°28.0'	4 ± 2	0.87 ± 0.12
1001M	1984	45	25°51,0'	47°49.8'	62 ± 3	1.47 ± 0.07
1006M	1984	20	25°37.7'	48°07.3'	138 ± 10	0.50 ± 0.05
1021M	1984	35	25°19.2'	47°29.0'	37 ± 3	1.07 ± 0.09
1025M	1984	15	25°06.0'	47°50.7'	34 ± 2	0.88 ± 0.09
1042M	1984	45	24°56.0'	46°59.0'	135 ± 11	0.42 ± 0.17
1047M	1984	15	24°25.5'	47°19.6'	46 ± 3	1.34 ± 0.04
4876	1986	14	23°37.4'	45°17.7'	38 ± 4	1.74 ± 0.06
4879	1986	41	23°50.2'	45°09.5'	227 ± 18	1.84 ± 0.08
4883	1986	82	24°06.4'	44°56.9'	108 ± 9	1.00 ± 0.10

ND - not determined

The mean deposition for Cs-137 varied from 2.3 to 17 $Bq.m^{-2}$ while for Pu-239+240 ranged from 0.03 to 2 $Bq.m^{-2}$. Both radionuclides present the same tendency of decreasing deposit values as the water depth increases. Figure 2 presents the mean deposits to different years of sampling. This study is going on, and samples collected in 1993 and 1997 are now being analyzed as well as the mineralogical composition of sediments.



( ) number of samples analysed

FIG.2. Pu-239+240 and Cs-137 mean deposits in sediments.

Data here reported represent reference values to our country and are very important because experimental values of artificial radioactivity deposition_are very sparce, specially to the South Atlantic. Data were compared with the expected inventory values from fallout to Southern Hemisphere, published at literature [3,4]. The brazilian southern coast seems to contain less artificial radioactivity than expected.

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PRESENT AND POTENTIAL CONTAMINATION OF THE RIVER SYSTEM AT MAYAK «PA»

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The nuclear installation at Mayak was built in 1948 and was the first installation in the former Sovjet Union to produce plutonium for use in nuclear weapons. Lack of technology and methods of treating large amount of radioactive waste led to releases of radionuclides directly into the open river system in the early years resulting in severe increase in radiation doses to the inhabitants along the river. To prevent further contamination of the river system a small natural pond (Lake Karachay) was used as repository in 1951, and two dams were built in the upper parts of the Techa River in 1956 and 1963. Two of the most serious accidents with nuclear material have occurred in Mayak. A waste tank exploded in 1957 resulting in severe contamination by radioactive material. A total of 20 villages and more than 10.000 people were evacuated. In April 1967 parts of Lake Karachay dried out and radioactive sediments were released with the wind covering a distance reaching up to 50-70 kilometres from Mayak.

The accumulated radioactive contamination at different locations in the vicinity of Mayak is listed in Table I. The data presents levels of contamination from the long-lived radionuclides cesium-137 and strontium-90.

TABLE I. ACTIVITY LEVELS IN THE ENVIRONMENT AT MAYAK, 1998 LEVELS (BASED ON [1]).

Localisation	Cs-137 + Sr-90 (PBq)
Lake Karachay	3900
Reservoir 17	66
EURT, Kyshtym-accident in 1957	0.72
Areas contaminated by the Karachay-accident in 1967	0.006
Reservoir No. 2,3,4,10,11	9.2
Asanov Swamp	0.22

Studies of mobility of radionuclides in environmental samples at Mayak show that strontium-90 is the most mobile of the relevant radionuclides and hence can be transported by river water. Cesium-137, although less mobile, can also be transported over large distances. The main source of river contamination today is the remobilization of strontium-90 from the boggy area at the upper reaches of Techa River (Asanov Swamp). Regular Russian monitoring programmes show that levels of strontium-90 leaving the swamp are three times higher than levels entering the swamp. The net outflow from the Swamp is now estimated to 2-3% of the 37 TBq of strontium-90 located in the swamp, 1992 levels [1].

The strontium-90 entering the Asanov Swamp mainly originates from leakage of contaminated water from Reservoirs 10 and 11 into the bypass channels. Some activity also enters the upper Techa through the bed of dam 11, however this source do contribute minor to the total flux of strontium-90. The contaminated groundwater in the vicinity of Lake Karachay has not yet resulted in increased levels in the nearby River Mishelyak which forms the upper part of the right bank channel.

Activity levels in groundwater collected from bore holes 3-4 km south of Lake Karachay showed large levels of strontium-90 and cobalt-60 with a maximum of 8800 Bq/l and 4200 Bq/l respectively [1]. The maximum concentration of strontium-90 in water was in the order of 0.01 % of the concentration in Lake Karachay. Cesium-137 were only found in low concentrations (maximum in the order of 10^{-6} % of the concentration in Lake Karachay) indicating that this radionuclide is much less mobile than strontium and cobalt. The contamination of the groundwater has increased significantly in the last decades [2]. Studies shows that effective remediation actions to reduce the water infiltration from Lake Karachay must be worked out within a maximum time period of 30-50 years.

Due to the amount of radioactive waste accumulated, Lake Karachay possess the largest potential for contamination of the river system. This may occur as a result of infiltration from contaminated groundwater, but also through surface runoff. Surface runoff may occur if contaminated water is spread due to natural catastrophes like thunderstorms or earth quake. However, such scenario will also be followed by severe local contamination. A future scenario may also be spreading of contaminated sediments from Lake Karachay if the lake dries out repeating the 1967 accident.

The water level in Reservoir 11 has increased steadily the last two decades resulting in concern for contaminated water leaving the top of the dam. An even more severe accident occur if the dam itself should break e.g. as a consequence of terrorist attack or earth quakes.

Increased resuspension of radionuclides, especially strontium-90, may occur from the Asanov Swamp during periods of flooding. Studies of binding properties of strontium-90 in water logged soils in the swamp showed that about 5% could be easily extracted with water and about 60% was extracted by NH_4Ac [1]. Hence, a large amount of strontium-90 present in the water logged soils may easily be transported with river water.

Accidents at technological storage tanks for liquid radioactive waste may lead to releases of radionuclides to the air. Such scenario may lead to sever contamination of the affected area.

Mayak PA are controlling the environmental contamination in the area and are putting large efforts into minimising the risk for accidental scenarios.

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ORGANOCHLORINE RESIDUES IN SEDIMENTS FROM SELECTED TRIBUTARIES TO MANILA BAY, PHILIPPINES

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Manila Bay, one of the Philippines' traditional fishing grounds, is located in the northwestern coast with an area of approximately 1,352 square kilometer and a coastline of 190 kilometer. Aquaculture activities in the Bay include the production of milkfish, *Tilapia*, prawns, oyster and mussel. However, tributaries to the Bay bring domestic sewage, solid wastes and agricultural and other chemicals from inland and aquaculture activities.

Sediment borne pesticides are the major route of transport of pesticides in the marine environment and benthic dwellers, filter feeders and the flora/fauna closely associated with the sediments could greatly be affected. This paper focuses on the monitoring of organochlorine pesticides in sediments collected from the mouth of rivers draining to Manila Bay and relate to the contribution of inland activities to the overall pollution of the Bay. Sediments from 14-25 tributaries (Figure 1) were collected in 1996 to 1998 and analyzed for the presence of HCB, aldrin, dieldrin, lindane, DDT, DDE, DDD, endosulfan I, endosulfan II and endosulfan sulfate using GLC-ECD.

DDE (0.3-8.9 ng/g), DDT (<0.5-0.8 ng/g), dieldrin (<0.2-1.4 ng/g), aldrin (<0.4 ng/g) and lindane (<0.4-1.3 ng/g) were detected in decreasing order of frequency during the end of the rainy season (December 1996) (Table 1). Only DDE (0.1 -0.4 ng/g) was detected during the start of the rainy season (June 1997) in 9 out of 22 rivers sampled. Aldrin (<0.4-11.3 ng/g), DDE (<0.4- 18.4 ng/g), HCB (<0.2-2.2 ng/g), DDD (<4.0-14.4 ng/g), lindane (<0.4-6.4 ng/g) and dieldrin (<0.2-0.5 ng/g) were detected in decreasing order during the middle of the rainy season (September 1997). Likewise, aldrin (<0.4-2.1), HCB (<0.2-1.2), DDD (<0.4-8.9) and lindane (<0.4-0.6) all in ng/g were detected in decreasing order of frequency during the end of the rainy season of January 1998. Aldrin (<0.4-3.6), DDE (<0.4-2.1), HCB (<0.2-0.3), lindane (<0.4-2.1) and endosulfan sulfate (<0.2-2.1) were detected during the dry season of May 1998.

The highest concentration of organochlorine pesticides in sediments (1996-1998) were detected in the mid wet season sampling of September 1997 except for dieldrin. The highest frequency of detection was also detected during the same time. This suggests that the possible source could be inland and brought about by the rains and into the Bay through its tributaries. Relatively DDT/DDE/DDD were detected in greater frequency in December 1996 and September 1997 sampling which corresponds to the end and mid wet season sampling, respectively (Table I). HCB and aldrin were mostly detected in September 1997 and January 1998 sampling, mid and end of wet season, respectively (Table II). Lindane was detected in 4 rivers and endosulfan sulfate in 7 rivers out of 23 rivers sampled in the middle of the wet season 1997. Only lindane is currently used in agriculture and is recommended for major crops like rice, sugarcane, pineapple and mango whereas endosulfan is restricted to institutional use only.

This study confirms the persistence and possible transport of organochlorine pesticides into the Manila via its tributaries. Although DDT has been banned for agricultural and for health uses, the detection of DDT and its metabolites indicate persistence and new sources which could means possible back door entry of this pesticide. Endosulfan is currently restricted for institutional use only, aldrin used to be used for termite proofing but is currently not marketed in the Philippines and lindane although available and recommended for a number of crops is not widely used. These organochlorine pesticides are still detected in the sediments collected in Manila Bay. However, both the Pampanga/Madamo river and the Angat/Tibaguin river which goes through rice fields from the mountains of Northern Luzon do not carry significantly higher pesticide residues in the sediments than other tributaries.

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AVOIDING POLLUTION IN SCIENTIFIC OCEAN DRILLING

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Scientific ocean drilling has been carried out in the world's oceans since the nineteen sixties. From 1968-83 the Deep Sea Drilling Project (DSDP), managed by the Scripps Institution of Oceanography in California under a contract with the US National Science Foundation, employed the drilling vessel Glomar Challenger for this purpose. In January 1985 the Ocean Drilling Program (GDP), operated by Texas A & M University, began operations with the drillship JOIDES Resolution which continue to this day. The principal funding agency remains the US National Science Foundation, but since its inception GDP has been an international program and currently receives financial support from 21countries.

The Ocean Drilling Program is a scientific research program whose objective is to recover cores and data from beneath the ocean floor in order to elucidate the history and evolution of the ocean basins and the nature of the underlying rocks. Scientific planning and direction for GDP, as for DSDP before it, is provided by the Joint Oceanographic Institutions for Deep Earth Sampling (JOIDES). Since the beginning of ODP nearly two thousand scientists from all the countries; supporting the program have participated in drilling legs on board the JOIDES Resolution.

The ODP operates globally and, as with DSDP before it, drills without a riser or blowout preventer in a wide range of geological environments. Water depths at GDP drill sites have ranged from 38 m to 5969 m, but are typically within the range 1000-5000 m. Depths of penetration at GDP drill sites, while generally less than 1000 m, have ranged up to 21 1 1 m below the sea floor. The drilling fluid is seawater, although occasional slugs of mud are circulated to clean or condition the hole. Thus drilling is carried out without well control, ie- without the ability to control pressures within the well. Because of the absence of well control, it is vital to ensure that the drillship does not drill into an accumulation of oil or gas. Drilling into a charged reservoir and causing oil or gas to escape into the marine environment is recognised as the main pollution hazard in scientific ocean drilling [1].

Avoiding drilling into hydrocarbon reservoirs is achieved by a twofold process: 1) All proposed drill sites are reviewed by an independent panel of experts in hydrocarbon exploration. The Pollution Prevention & Safety Panel (PPSP) was formally established a; part of the JOIDES advisory structure in 1970, soon after the Stan of DSDP. The PPSP is composed of geologists, geochemists, geophysicists and drilling engineers from the petroleum industry, government and academia. Scientific proponents of drilling assemble pertinent information relating to their proposed sites, including seismic profiles, geological interpretations, data from nearby drillsites where available....and present it to the PPSP. Sites which are located over potentially hydrocarbon-bearing structures are either rejected or, if possible, moved to safer locations off-structure. Thus the effect of the PPSP scrutiny is to give GDP a site selection process which is the inverse of that used by the offshore industry in exploration drilling. Industry is trying to find hydrocarbons at every well that it drills; GDP is trying to avoid encountering hydrocarbons. 2) All cores recovered to the drillship are monitored for hydrocarbons. This is possible because the JOIDES Resolution is not just a drillship, but a sophisticated floating laboratory with the scientific and technical manpower to run it. At the present time the equipment in the ship's chemical laboratory include; three gas chromatographs, a Rock Eval, and a Geofina Hydrocarbon Meter, among a host of other equipment. Thus sophisticated analyses of the hydrocarbons present in the cores can be carried out on board ship. Some of these analyses can be carried out very quickly (~ 30 minutes), so that their outcome is available for operational decision-making- The PPSP has issued guidelines to help shipboard personnel to distinguish between gas of biogenic origin, which is often present in marine sediments, and gas of thermogenic origin which has migrated to the vicinity of the rocks being cored [1]. The presence of mature migrated hydrocarbons in the cores is taken as an indication that a reservoir is being approached and drilling is stopped. The PPSP guidelines also recommend plugging and abandonment procedures, according to the geological environment, for the holes that ODP drills.

This two stage process has been wholly successful in preventing ODP land DSDP before it) from releasing unwanted hydrocarbons into the marine environment. In practice, very few holes have been terminated because increased concentrations of thermogenic hydrocarbons have been detected - about half a dozen holes at the nearly five hundred sites that ODP has drilled since January 1985. For example, increasing concentrations of gases in the propane-pentane range, inferred to be of thermogenic origin, were observed near the bottom of ODP Hole 909C [2]. The drilling of this hole was terminated at 1062 m below the sea floor on the basis of these data [3].

The existence of methane hydrate in the sediments of the ocean floor has been known for more than twenty years, In water depths of more than a few hundred metres, the temperature and pressure conditions allow gas hydrate to be stable to tens/hundreds of metres below the sea floor. Gas hydrates are particularly prevalent on continental margins, and are often associated with a bottom-simulating reflector (BSR) on seismic records. Studying gas hydrates is an important objective of ODP, since methane is a greenhouse gas which may play a significant role in climate change. It has also been proposed that gas hydrates could be an important future energy resource. Thus over the past decade the PPSP has been presented with a number of proposals to drill though BSRS [4].

Up to about ten years ago BSRS were interpreted as marking the base of the gas hydrate stability zone and as a seal for possibly high pressure gas beneath. Thus the PPSP at that time did not allow the drilling of holes which penetrated a BSR. Thermodynamic arguments then demonstrated that the gas beneath a BSR was most likely not overpressured but at hydrostatic pressure. The PPSP therefore adopted a gradual and cautious approach to allow penetration of BSRS. BSRS have now been penetrated at about a dozen sites in three widely-separated geographical areas without encountering any drilling difficulties or evidence for overpressured gas.

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XA9952091

EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT OSPARCOM REGION - NORTH SEA

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Euro Chlor has voluntarily agreed to carry out environmental risk assessments of 25 chemicals, related to the chlorine industry. The assessments were carried out specifically for the marine environment, according to the methodology laid down in the EU risk assessment Regulation (1488/94) and the Guidance Document of the EU New and Existing Substances Regulation (TGD, 1997). The study consists of the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests which have been evaluated according to the quality criteria recommended by the EU (Guidance Document). Exposure data have been derived from analytical monitoring programs in large rivers and estuaries in the North Sea area. Finally the risk is indicated by the ratio of the "predicted environmental concentrations" (PEC) and the "predicted no effect concentrations" (PNEC) for the marine aquatic environment. To determine the PNEC value, three taxonomic groups representing key trophic levels have been considered: aquatic plants, invertebrates and fish.

The risk assessments have been completed for five chemicals. The results will be summarized hereafter.

For 1,2 dichloroethane (EDC) 21 studies for fish, 17 studies for invertebrates and 7 studies for algae have been evaluated. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 1100 µg/l. Most of the available monitoring data apply to rivers and estuaries and were used to calculate PECs. The most recent data (1991-1995) support a typical PEC of 0.5 µg EDC/l and a worst case PEC of 6.4 µg EDC/l. The calculated PEC/PNEC ratios give a safety margin of 170 to 2200 between the predicted no effect concentration and the exposure concentration.

For 1,1,2-trichloroethane (T112) 22 studies for fish, 45 studies for invertebrates and 9 studies for algae have been evaluated. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 300 µg/l.

Most of the available monitoring data apply to rivers and estuaries and were used to calculate PECs. The most recent data (1991-1995) support a typical PEC of 0.01 µg T112/l water and a worst case PEC of 5 µg T112/l water. The calculated PEC/PNEC ratios give a safety margin of 60 to 30,000 between the predicted no effect concentration and the exposure concentration.

For trichloroethylene (TRI) 19 studies for fish, 30 studies for invertebrates and 14 studies for algae have been evaluated. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 150 µg/l.

Most of the available monitoring data apply to rivers and estuaries and were used to calculate PECs. The most recent data (1991-1995) support a typical PEC of 0.1 µg TRI/l water and a worst case PEC of 3.5 µg TRI/l water. The calculated PEC/PNEC ratios give a safety margin of 40 to 1,500 between the predicted no effect concentration and the exposure concentration.

For tetrachloroethylene (PER) 18 studies for fish, 13 studies for invertebrates and 8 studies for algae have been evaluated. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 51 µg/l.

Most of the available monitoring data apply to rivers and estuary waters and were used to calculate PECs. The most recent data (1991-1995) support a typical PEC of 0.2 µg PER/l water and a worst case PEC of 2.5 µg PER/l water. The calculated PEC/PNEC ratios give a safety margin of 20 to 250 between the predicted no effect concentration and the exposure concentration.

For chloroform (CLM3) 23 studies for fish, 17 studies for invertebrates and 10 studies for algae have been evaluated. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 72 µg/l (or 1 µg/l for sensitive species). Most of the available monitoring data apply to rivers and estuary waters and were used to calculate PECs. The most recent data (1991-1995) support a typical PEC of 0.2 µg chloroform per litre of water and a worst case PEC of 5 to 11.5 µg chloroform per litre of water. The calculated PEC/PNEC ratios give a safety margin of 6 to 360 between the predicted no effect concentration and the exposure concentrations. Sensitive species may however be at risk under worst case conditions.

Additional evaluation of their environmental fate and bioaccumulation characteristics showed that no concern for food chain accumulation is expected.

In the past these compounds have been subject to various emission reduction programmes [4].

With respect to the present day use volumes, use patterns and related emissions it can be concluded based on the abovementioned studies that none of these five compounds represent a risk to the marine aquatic environment in the area of the North Sea.

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XA9952092

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PLUTONIUM AND POLONIUM CONCENTRATIONS IN THE DIFFERENT WATER MASSES CROSSING THE STRAIT OF GIBRALTAR

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The exchange waterflows circulating through the Strait of Gibraltar serve to balance the water deficit and salt content of the Mediterranean sea, a semi-enclosed basin. Both the inflowing Atlantic water and the outpouring Mediterranean layer might deliver a wide range of elements and compounds either dissolved or attached to the floating particulate matter. A better knowledge of the exchange fluxes between the two basins would be helpful to track down the transport pathways and final fate of a broad spectrum of natural and antrophogenic radionuclides.

In this paper total Pu and Po concentrations in the water column are presented as part of a study to determine the exchange fluxes and overall budget of these selected nuclides within the Atlantic and Mediterranean basins. Polonium is a natural radionuclide continously input to the sea via atmospheric deposition from the radon existing in the air. Plutonium is a man-made radionuclide that was mostly introduced in the atmosphere during the 60's nuclear testing . Since then, it has been gradually dissapearing due to fallout and the banning of nuclear atmospheric explosions.

Sea water samples (not filtered) at different depths were collected in June 1997 at several stations located on both sides of the Strait of Gibraltar, to determine the $^{239+240}$Pu , ^{210}Po, and ^{210}Pb distribution profiles. The different water masses co-existing in this Strait were identified by continously employing the CTD (conductivity and temperature detector). As a basic approach, the Atlantic water salinity dropped below approximately 36.5 ‰ and the Mediterranean flow showed salinity values above 37.5 ‰.

<u>Polonium-210</u> : Polonium was pre-concentrated in 20 liters water samples. Sea water was acidified with concentrated HCl (25%) to pH 1-2. The ^{209}Po tracer and Pb and Co carriers were added for later calculation of the chemical recovery and to form the complex (APDC-Co). Polonium was scavenged from the water by quantitative co-precipitation with the chelate cobalt-ammonium pyrrolidine dithiocarbamate (Co-APDC). After collection of the precipitate by filtering, the filters were stored in plastic bags for later processing in the laboratory with standarised methodology [1]. The average chemical recovery for these samples was 98±6 (n=18) .

<u>Plutonium-239+240</u>: Sea water samples of 110 liters were brought to pH 1-2 with 370 ml of concentrated HCl (25%), then the ^{242}Pu tracer was added. The water was stirred during two hours to achieve equilibrium between the tracer and the plutonium from the sample. Then, 1 g of Fe(III) was added and neutralized to pH= 8-9 with NaOH (20%) to favour the co-precipitation of plutonium with the $Fe(OH)_3$. The solution and precipitate were stored for 4-5 hours allowing the precipitate to decant. The remaining solution was filtered in glass-filters. These filters were stored in plastic bags for further analysis in CIEMAT laboratories with standarised methodology [2]. The average chemical recovery for these samples was 64±6 (n=18)

Po and Pu concentrations results versus salinity are presented in Fig. 1. Total $^{239+240}$Pu concentrations ranged from 8 to 14 mBq/m^3 in the Atlantic waters. The lowest values were found on the most western part of the Strait gradually increasing while crossing it eastwards. This variation in activities had been previoulsy observed [3], with Pu concentrations ranging from 5-6 mBq/m^3 on the Atlantic part of the Strait, and from 8.5-16 mBq/m^3 on the eastern section.

Mediterranean outflowing water shows concentrations ranging from 18-25 mBq/m^3 . These results are slightly smaller than those obtained in the bibliography (16-35 mBq/m^3) , but in a reasonable good agreement [4]. Therefore, it could be suggested that inflowing Atlantic waters seem to be Pu-depleted, whilts the Mediterranean layer appears to be Pu-enriched. Global fallout from atmospheric tests is the source term of the measured Pu, as the mean ratio ^{238}Pu/$^{239+240}$Pu (0.08) indicates.

^{210}Po concentration values ranged from 1.0 to 1.9 Bq/m^3 in inflowing Atlantic waters and from 0.4 to 0.9 Bq/m^3 in outpouring Mediterranean flow. The Eastern part of the Strait shows lower Po activities than the western section. Opposite to the results of Pu, Atlantic waters are enriched in this radionuclide and Mediterranean waters are depleted. The upper layer formed by Atlantic water receives recent atmosferic Rn inputs, meanwhile, the deeper Mediterranean water allows ^{210}Po to decay (T $_{1/2}$= 22.16 years) while moving downwards in the water column.

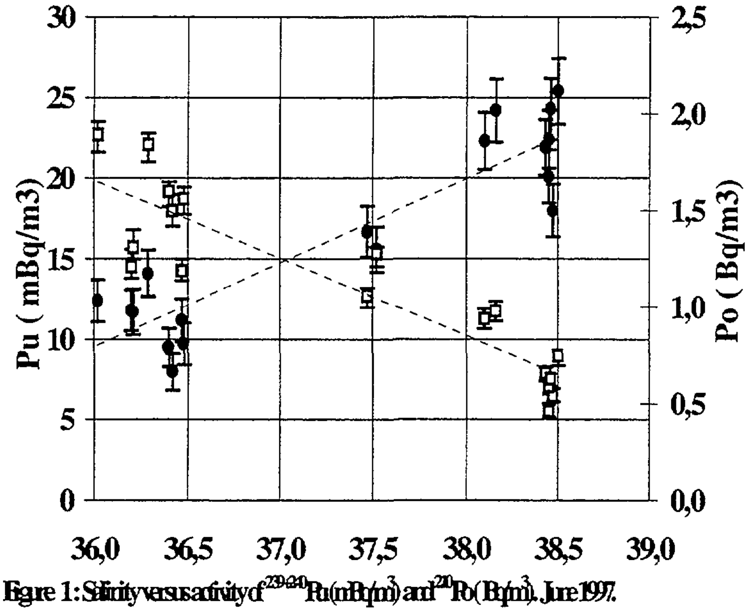

FIG. 1. Pu and Po concentrations vs. salinity.

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TRANSPORT OF RADIONUCLIDES IN THE KARA SEA AND EASTERN BARENTS SEA

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The Arctic seas are influenced by radioactive contamination from military and civilian sources such as global fallout, discharges from reprocessing plants, river transport and the Chernobyl fallout. Potential sources are dumped radioactive waste in the Kara Sea [1]. A joint Norwegian American field expedition to the Kara Sea was carried out in August-September 1995. An expedition to the Eastern Barents Sea was conducted in September 1996. The investigations were funded by The Norwegian Defence Research Establishment, The Norwegian Ministry of Defence and US Office of Naval Research. Both expeditions were conducted on the Norwegian Defence Research establishments ship *H U Sverdrup II.*

The results from these expeditions are presented by [2, 3, 4, 5, 6]. The dominating features of ocean circulation in the Kara Sea are two large anticyclones. One covers the Ob and Yenisey Delta, extending westward over the East Novaya Zemlya Trough, and a second anticyclone is in the south-western basin. The anticyclone over the delta, (about 300 km diameter), carries river water westward over the East Novaya Zemlya Trough and then northward into the area of the Persey Current, north of Novaya Zemlya. We suspect that the leftward turning river water is a relaxation from the impulsive June outflow into a semi-confined basin [6]. The northward current next to Novaya Zemlya has also been observed in an earlier survey [7] and is contrary to present Russian Atlases of surface currents. The left turning, (cum sole), discharge from the rivers is substantial in the temperature/salinity maps, in ice beacon drifts and in satellite images..

The nuclear reactor dumped on a barge in the East Novaya Zemlya Trough was located with echo sound at 350 m depth in the position 72:17,99 N and 57:38,20 E. No leakage of radionuclides from this reactor or other local sources were detected. The levels of ^{137}Cs and ^{90}Sr in the Kara Sea are low and very low in the Eastern Barents Sea, while the levels of ^{239,240}Pu are similar and mainly reflect global fallout. The average levels of ^{137}Cs in sea water and sediments are significantly higher in the Kara Sea than in the Eastern Barents Sea, the levels of ^{90}Sr are also generally higher in sea water from the Kara Sea than the Eastern Barents Sea as can be expected from the influence of river transport. Vakulovsky has also documented that river transport of ^{90}Sr to the Kara Sea is significant source at the same level as global fallout [8]. The levels of ^{90}Sr and ^{239,240}Pu in sediments appear to be the same in the Kara Sea and Eastern Barents Sea. Sea water collected in the Eastern Barents Sea were subjected to sequential cross-flow filtration immediately after sampling (0.45 µm and 10.000 Da) to determine possible attachment to particles and colloids. All ^{90}Sr present was dissolved and no attachment to colloids were detected. The levels of ^{137}Cs and ^{90}Sr in sea birds from different regions of the Kara Sea were found to be very low. The decay corrected ^{238}Pu/^{239,240}Pu isotope ratio was estimated to 0.03 which correlates to global fallout activity ratio in the northern hemisphere of 0.03 [9].

TABLE I. AVERAGE CONCENTRATIONS OF ^{137}Cs, ^{90}Sr AND ^{239,240}Pu OF SURFACE AND BOTTOM WATER, (Bq/m^3, ^{239,240}Pu: mBq/m^3), AND SEDIMENTS, (Bq/kg), OF THE KARA AND EASTERN BARENTS SEAS

	Kara Sea	Eastern Barents Sea
^{137}Cs surface water	5.7	4.4
^{137}Cs bottom water	8.6	3.2
^{137}Cs sediments	15.3	6.5
^{90}Sr surface water	3.3	1.8
^{90}Sr bottom water	1.8	1.4
^{90}Sr sediments	0.6	0.7
^{239,240}Pu surface water		12
^{239,240}Pu bottom water		15
^{239,240}Pu sediments	0.6	0.7

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THE FLUX OF PARTICLES AND CONTAMINANTS IN THE SKAGERRAK

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The Skagerrak, located off southern Norway, is an important part of the North Sea ecosystem and is the transition zone between the North Sea and Kattegat-Baltic Sea. The Skagerrak is highly productive and an important feeding and breeding area for fish, landings of which amount to approximately 300 000 tonnes annually. It is also one of the most beloved and commercially important recreational areas in Norway. Its geographical location makes it a conduit not only for ship traffic but also for agricultural and industrial wastes.

Particles provide some of the most important biogeochemical pathways for contaminant transport in coastal waters like the Skagerrak. Thus, the present investigation addressed the influx and fate of particulate biomass and persistent organic pollutants (POPs) such as some polycyclic aromatic hydrocarbons (PAHs). The occurrence of POPs in the Skagerrak is of special concern due to their toxicity, persistence and lipophilic properties, resulting in bioaccumulation and biomagnification through the food web up to humans. POPs (and other contaminants like radionuclides and fertilizers) enter the Skagerrak via the atmosphere and terrestrial runoff either directly or by advection into the area from the North Sea in the west or Kattegat-Baltic Sea in the east. In fact, the North Sea Task Force stated in 1993: "Since 50 - 70% of the suspended matter in the North Sea is deposited in the Skagerrak this area acts as the dustbin of the North Sea. Elevated values of PCBs and PAH in sediments and deep water fish species [have] been registered in the Norwegian Trench [Skagerrak]".

A field study in the Skagerrak from winter 1997 through to early spring 1998 investigated particle fluxes due to both bottom sediment resuspension and a surface phytoplankton bloom, presumably the two most important particle transport avenues in this area. Field activities included deployment of a daily as well as long-term moored sediment-trap/current-meter rig, benthic-boundary-layer (BBL) sampling, hydrocast sampling and sediment sampling. Parameters of measurement included: Water column - CTD, nutrient salts, oxygen; Water column, sediment traps, BBL, sediments - POC, PON, seston, chlorophyll *a* and pheopigments, grain size, ^{234}Thorium, PAHs, PCBs, DDT (and derivatives), and ^{137}Cesium.

Results indicated that during the winter, the current velocity near the sea floor strongly influenced the rates of deep sedimentation of both particles and contaminants. This was due largely to the resuspension and subsequent advection of sediments. Biological effects on particle and contaminant transport were readily documented during this investigation, however they were secondary to physical influences, partially because of the presumably low rates of pelagic productivity in the months of investigation.

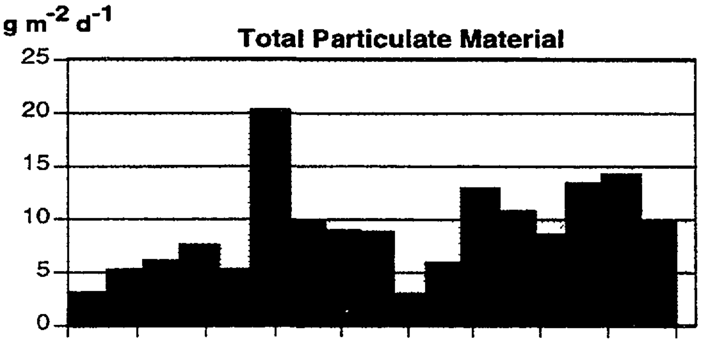

FIG. 1. Sedimentaton rates of total particulate material in the deep Skagerrak from 17 Dec 97 to 17 March 98

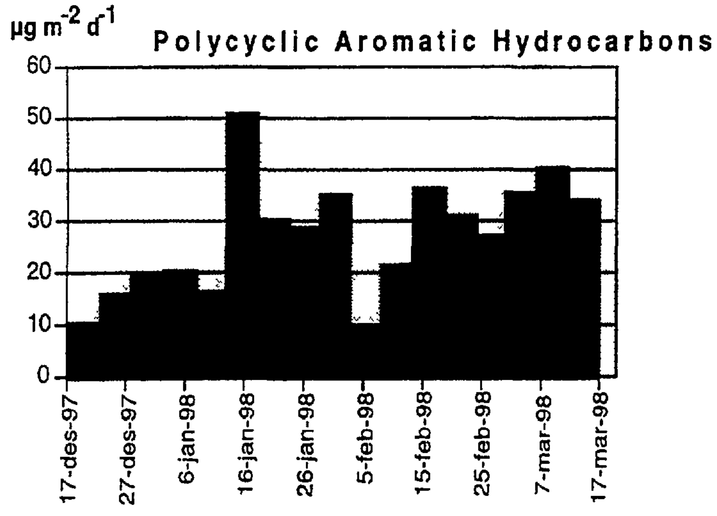

FIG. 2. Sedimentaton rates of polycyclic aromatic hydrocarbons in the deep Skagerrak from 17 Dec 97 to 17 March 98.

The association of PAHs with the sedimentation of other particulate biomass was strong, whereas the sparseness of data for ^{137}Cs made it difficult to draw reliable conclusions. Estimates for the distribution of particulate biomass and PAHs indicated that the amount suspended in the water column can be similar to that deposited in a 1-cm thick layer of surface sediments. The concentrations of particles and PAHs in the BBL were particularly high. Notably, the concentrations of PAHs in the sediment traps were generally higher than in the surface sediments.

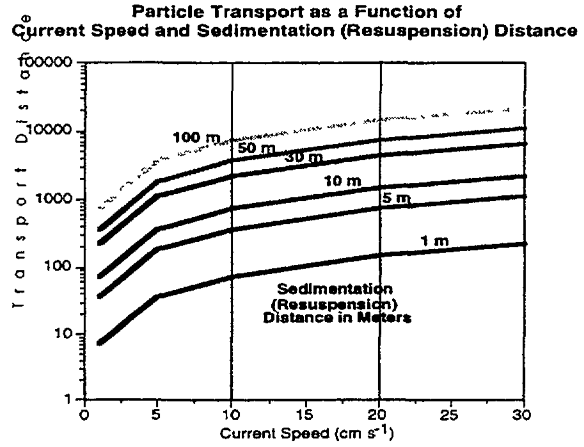

FIG 3. Potential horizontal transport distances for a typically sized particle (spherical, 4.21 µm in diameter and a density of 1.20 g cm-3) in relation to current speed and the vertical sedimentation distance.

Estimations for the sinking speeds of mean sized particles measured in our investigation indicate that typical Skagerrak currents can potentially transport these particles many thousands of kilometers. However, under conditions of particle aggregation as well as sedimentation accompanied by particle scavenging, it is suggested that large amounts of particles and contaminants are rapidly deposited at the sediments or in the benthic boundary layer. This is an important feature which has yet to be tested.

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THE LESSONS LEARNT FROM A SERIES OF RADIOACTIVITY MEASUREMENT INTERCOMPARISON EXERCISES

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Over the past decade, the National Physical Laboratory (NPL) has run a number of intercomparison exercises, aimed at those laboratories making measurements of radioactivity at environmental levels.

The need for such intercomparisons were initially driven by the Chernobyl accident and it's aftermath. Immediately after the accident, many measurements were made of radioactivity in the UK environment, but the lack *at that time* of a coordinated programme of measurements, feeding into a dissemination centre did nothing to improve public confidence in such measurements. This situation was remedied by the Department of the Environment (DoE) in the years following Chernobyl. In the longer term this perceived (and in most cases, undeserved) lack of public confidence in 'official' data led many laboratories in the UK, with no statutory need to measure radioactivity, to equip themselves to be able to make measurements of radioactivity in food and other environmental materials.

However, there were no national schemes to monitor the quality of such measurements and in 1989 the Department of Trade and Industry (DTI) asked NPL to organise such an intercomparison. The samples sent out for the first exercise contained ^{90}Sr, ^{106}Ru, ^{134}Cs, and ^{137}Cs at levels of 100-1000 Bq/kg. Since then, the exercises have grown in scope and complexity; there are now up to 9 γ-emitters included in the gamma-spectrometry samples and the samples for radiochemical analyses contain a range of α- and β-emitters; the activity levels are a factor of 10-100 lower. Most of the exercises have involved purely aqueous samples, although a liquid milk and a spiked kaolin sample have been included in past exercises. Samples are sent out to those who order them (the exercise is open to any laboratory in the world), along with data reporting forms and a timetable for the exercise. The data returned to NPL is analysed and presented in a report that is placed in the public domain, although the participants anonymity is preserved. The final part of the intercomparison exercise is to hold a meeting for participants at NPL, where the data are discussed by the participants and NPL staff to see what lessons have been learnt and to suggest the form of the next exercise.

A number of lessons have been learnt over the years, both by the participants and the organisers! To illustrate this, the results for several nuclides over the series of intercomparisons will be reviewed. However, the main points are as follows. To begin with, it was clear that there was little appreciation of the finer points of γ-spectrometry by a number of laboratories. this manifested itself in different ways. It was clear from the results submitted for ^{134}Cs that there was a low bias of 5-10%. This was attributable to the phenomenon of cascade summing, but this was not considered by most participants in the initial exercises. Results for this nuclide, but there is now a greater appreciation of the effect by measuring laboratories, although few have the resources to make an accurate correction. The use of inappropriate calibration standards was also widespread in the initial exercises, although the situation has now been entirely rectified, with participants using a liquid 'mixed radionuclide' source for detector calibration. There is an ongoing debate about the sources of suitable nuclear decay data. Again in the initial exercises, there were many sources of data used, some of which dated back to the 1950's and which are clearly inaccurate. There is a better appreciation of what data sources to use, but there is a marked reluctance on the part of manufacturers of equipment to divulge their sources of data that they distribute and this compromises the ability of the user to comply with the requirements of accreditation schemes.

For our part, we have found that a minimum of data should be collected, but this should be sufficient to make the data analysis of the exercise meaningful as well as allowing NPL to review trends over time. furthermore, as the organiser, it pays to keep the exercise as simple as is required by the user community and able to trace all the contributing data throughout the exercise.

The exercises that we run are well subscribed each time they are run and provide NPL, the users and the United Kingdom Accreditation Service (UKAS) with valuable information about the ability of UK laboratories to measure low levels of radioactivity and act as a source of education to all those taking part. They will continue for the foreseeable future and will continue to be of interest to the participants, NPL and UKAS.

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DYNAMICS OF PARTICLE SEDIMENTATION IN THE OPEN NW MEDITERRANEAN SEA

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As part of the DYFAMED program (DYnamique des Flux en MEDiterranée) the downward flux of particles, carbon and other elements has been studied in the open northwestern Mediterranean Sea since 1987. Also, during the last few years biological (primary) production using the *in-situ* ^{14}C incubation method has been measured and the vertical distribution of large particulate material and aggregates in the water column assessed by an underwater video profiler in order to relate sedimentation to surface production. The primary objective of the experiment is the observation and prediction of biogeochemical cycles of particles and associated compounds through long-term study in the central Ligurian Sea, where biological productivity ranges from oligotrophic to mesotrophic. Since these characteristics are observed over large areas of the ocean, the DYFAMED site can be considered as a model area. Particle flux is especially important in controlling the vertical transport and cycling of contaminants such as particle reactive radionuclides, metals and organochlorine compounds [1].

The measured particulate and carbon fluxes displayed a marked seasonal pattern with mass fluxes usually maximal during winter and carbon fluxes normally highest in late spring [2]. Carbon fluxes in winter were also elevated but not as high as those measured during the spring. In general, mass and carbon fluxes were lowest in late summer and autumn, with the organic carbon flux pattern closely following that for total carbon. At 200 m depth, the mean particle flux measured during a 7 year period (1987-spring 1991 and mid 1993-1995) was 80 mg m^{-2} d^{-1} and ranged from a minimum of 5 in summer to a maximum of 335 mg m^{-2} d^{-1} in winter (Fig. 1). Carbon flux was relatively high with a mean value of 14 mg m^{-2} d^{-1} (range, 2 to 68 mg m^{-2} d^{-1}). About 80% of the sedimenting carbon was of organic origin. The observed fluctuations over the year were considerable and varied by a factor of up to 60. At 1000 m, mean mass fluxes were only 40 % of those at 200 m depth whereas organic carbon fluxes represented 30% of those in surface waters. This difference results from a rapid degradation of the sedimenting particles in the water column, with a preferential recycling of the organic fraction resulting in a decrease of carbon content of the particles. Carbonate carbon concentration did not change significantly with depth. On an annual basis, total mass and particulate carbon flux leaving the surface layers were 30 and 5.1 g m^{-2} a^{-1}, respectively, of which 4.0 g m^{-2} a^{-1} was organic (POC) and 1.1 g m^{-2} a^{-1} consisted of carbonate carbon.

Primary production in surface waters was highest in late winter and early spring with the development of diatom populations and in April with the bloom of flagellates (0.5 to 2.0 µg C m^{-2} d^{-1}). Also, concentrations of particles and aggregates larger than 150 µm in the water column were highest from winter to late spring (60 to 90 particles l^{-1} at 50 m and 10 to 40 particles l^{-1} between 200 and 1000 m depth) and lowest in summer (<10 particles l^{-1} in the entire water column). Thus, measured particle fluxes co-varied with biological production and suspended particulate concentrations in the water column. Examination of the organic compounds in the particles (*n*-

alkanes, fatty acids) indicates that, at 200 m, the settling organic material in winter was characterized by a high proportion of refractory (old) organic matter and a low content of more labile (fresh) carbon. During the spring and summer period, fluxes contained undegraded phytoplankton and zooplankton detrital material [3]. In the deeper trap samples, refractory organic matter was still present, but the fresh input was very low and had evidently been consumed in the upper water column. The implications for rapid transport of contaminants to depth in the region are discussed.

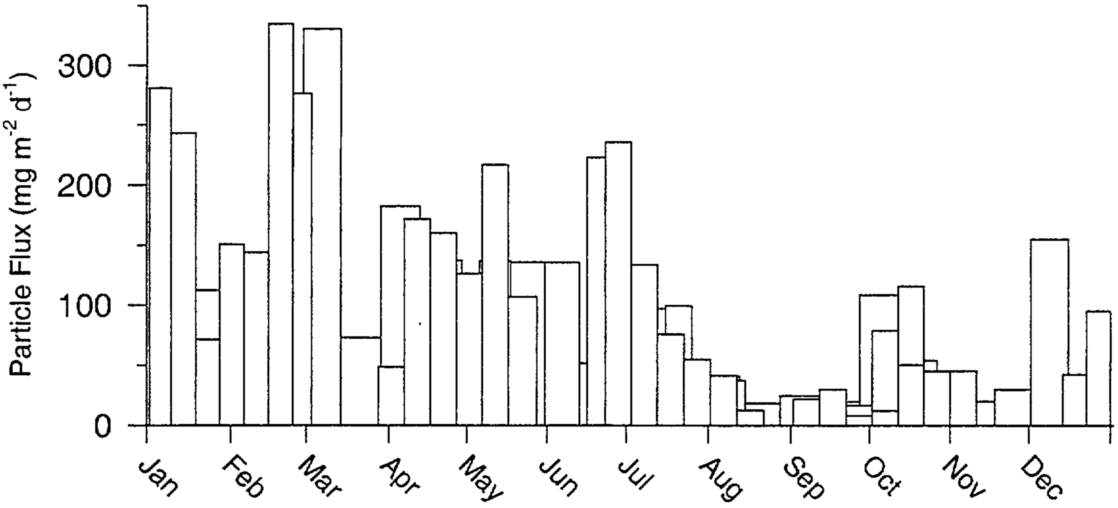

FIG.1. Vertical flux of particles at 200 m depth at the DYFAMED site (43°25 N, 7°52 E, northwestern Mediterranean Sea) over a 4 years period.

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ARTIFICIAL RADIOACTIVITY IN CARLINGFORD-LOUGH, IRELAND

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The routine discharges of low-level liquid waste from the British Nuclear Fuels reprocessing plant at Sellafield in Cumbria have resulted in enhanced concentrations of artificial radioactivity in the Irish marine environment, particularly along the north-east coast. During 1990 a detailed study of levels of artificial radioactivity in Carlingford Lough, a sea Lough in which a significant number of commercial shellfish producers are located (Figure 1), was carried out. The aim of this study was to determine whether radioactivity concentrations in environmental materials from the Lough were enhanced above those found elsewhere along the north-east coast. The study concluded that concentrations in the Lough were broadly similar to those measured elsewhere along this coast [1]. In 1994, the discharge authorisations for Sellafield were revised, resulting in increased discharges of some radionuclides including technetium-99 [2]. In October 1997 a follow-up to the original study was carried out by the RPII and the EHS to determine the current concentrations of artificial radioactivity in the Lough and to assess the effects of Sellafield discharges on the region following the revision of the certificate of authorisation.

Samples of seawater, seaweed, inter-tidal sediment, lobsters, mussels, oysters and winkles were collected from 9 coastal sites and 4 sites within the Lough. All samples were analysed for caesium-137 and other gamma emitting radionuclides and a selected number of samples for technetium-99, plutonium-238, plutonium-239,240 and americium-241 using standard radiochemical techniques [2].

The data obtained from this study and other routine monitoring of the area during 1997 are summarised in Table 1. When compared with data from the 1990 study [1], it is clear that there has been a decrease in Cs-137 activity concentrations in the region. For example, the mean Cs-137 activity concentration measured in seawater decreased from 0.092 Bq/l in 1990 to 0.040 Bq/l in 1997. A similar decrease was observed in other marine compartments, for example, the mean Cs-137 activity concentration measured in seaweed in 1990 was approximately 33 Bq/kg (dry), compared to 8.3 Bq/kg (dry) in 1997. This trend is comparable with that observed at other east coast sampling sites and reflects the decreased discharges of this radionuclide from Sellafield. The increased discharges of technetium-99 from Sellafield since 1994 have resulted in an increase in the measured activity concentration of this radionuclide at all east coast sampling sites [2]. For example, the mean activity concentration of this radionuclide in seaweed from the Lough in 1994 was 345 Bq/kg (dry), this increased to 5720 Bq/kg (dry) in 1997. This is similar to the increase observed at other east coast sites for this period [2]. The activity concentrations of technetium-99 measured in samples from the Lough did not differ significantly from those measured at other locations on the north-east coast during 1997.

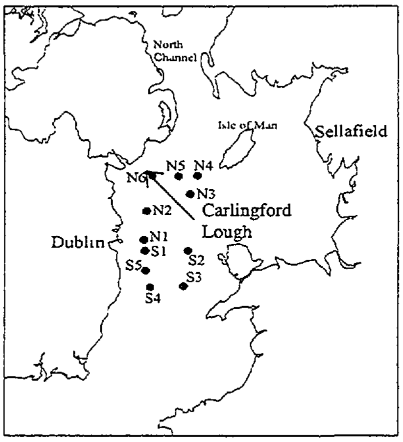

FIG. 1. Location of Carlingford Lough.

This is true of the measured activity concentrations of all other artificial radionuclides determined [2, 3]. These data were used to assess the dose due to seafood consumption, recreational and work uses of the area. A "critical individual" was postulated, as a hypothetical person who spends 100 hours/year swimming, 1000 hours/year on intertidal areas and ingests 10 g of sand/year. It was also assumed that this same individual consumes 50 kg fish/year, 10 kg crustaceans/year and 10 kg molluscs/year. A model developed by Hunt [4], dose conversion factors recommended by the International Commission on Radiological Protection [5] and 1990 data [1] were used to calculate the doses to the "critical individual" for both 1990 and 1997. These are summarised in Table 2. The clear decrease in the annual dose between 1990 and 1997 is mainly attributable to the reduced activity concentration of Cs-137 in the environment and occurs despite the increased discharges of technetium-99. These doses are of negligible radiological significance and can be compared to the annual average dose of 2,500 – 4,000 μSv received by members of the public from all sources of radiation [1].

TABLE I. RADIOACTIVITY IN ENVIRONMENTAL MATERIALS FROM CARLINGFORD LOUGH, 1997

Sample	Mean Activity Concentration Bq/kg, wet weight				
	Cs-137	Tc-99	Pu-238	Pu-239,240	Am-241
Seawater	0.040	0.045	nm	nm	nm
Seaweed[1]	8.3	5720	0.39	2.2	1.2
Sediment[1]	25.0	nm	1.2	7.5	4.1
Fish	1.0	0.49	0.0001	0.0003	0.0003
Lobster	0.53	225	nm	nm	nd
Mussels	0.70	29.0	0.032	0.17	0.11
Oysters	0.30	7.1	0.019	0.098	nd
Prawns	0.90	72	0.0072	0.040	0.14
Winkles	0.46	19.5	0.035	0.20	0.15

Note: 1. Bq/kg, dry weight nm = not measured nd = not detected

TABLE II. COMMITTED EFFECTIVE DOSES DUE TO ARTIFICIAL RADIOACTIVITY IN CARLINGFORD LOUGH

Dose pathway	1990 (μSv)	1997 (μSv)
Seafood ingestion - "critical individual"	7.0	2.6
External dose + sediment ingestion - "critical individual"	6.9	2.5

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CHARACTERIZATION, IMPACT AND FATE OF ATMOSPHERIC INPUTS IN THE WATER COLUMN

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The transport of matter by the atmospheric pathway is responsible for an efficient spreading of many compounds to the sea [1]. Owing to its relatively reduced dimensions (surface area : 8.4 10^5 km^2), as well as numerous and intense land-based emission sources along its shores, the western Mediterranean basin is particularly subjected to particulate and dissolved atmospheric inputs, whether they are of anthropogenic origin or natural pulsed inputs such as Saharan dust events [2,3].

Total atmospheric fluxes in the northwestern Mediterranean Sea have been already described for several compounds among which trace metals [2,4]. Some marine flux data restricted to continental shelf waters or nearshore coastal waters exist in the Mediterranean Sea (see review in [5]). However, long-term observations on marine fluxes are still lacking in open Mediterranean waters. Consequently, data dealing with concomitant atmospheric and marine fluxes are also lacking. The coupling of an atmospheric sampling site with a marine sampling site should improve the knowledge of transfer processes of atmospheric inputs to the deep water layer, and also bring more indications on the potential fertilization of the surface waters by atmospheric inputs.

Processes of downward transfer in the water column are presumably governed by biological activity [6,7], itself depending on hydrological (seasonal stratification of waters) and meteorological conditions (wind events, sunniness). The description and quantification of the different (dissolved + particulate) atmospheric loadings is the preliminary step for assessing the fate of atmospheric matter in the water column (in the present work, sediment trap data at 200 and 1000 m depths are not available yet). Trace metals constitute good indicators of process studies for the biogeochemical response of the marine environment to external constraints [8].

The present results, obtained from continuous sampling (wet, dry and total inputs) at the Cap Ferrat sampling station (Ligurian Sea) enable to quantify the dissolved and particulate fractions relative to various types of metals (dust-derived, anthropogenic, medium). Figure 1 illustrates three typical behaviours, always linked to the emission sources.

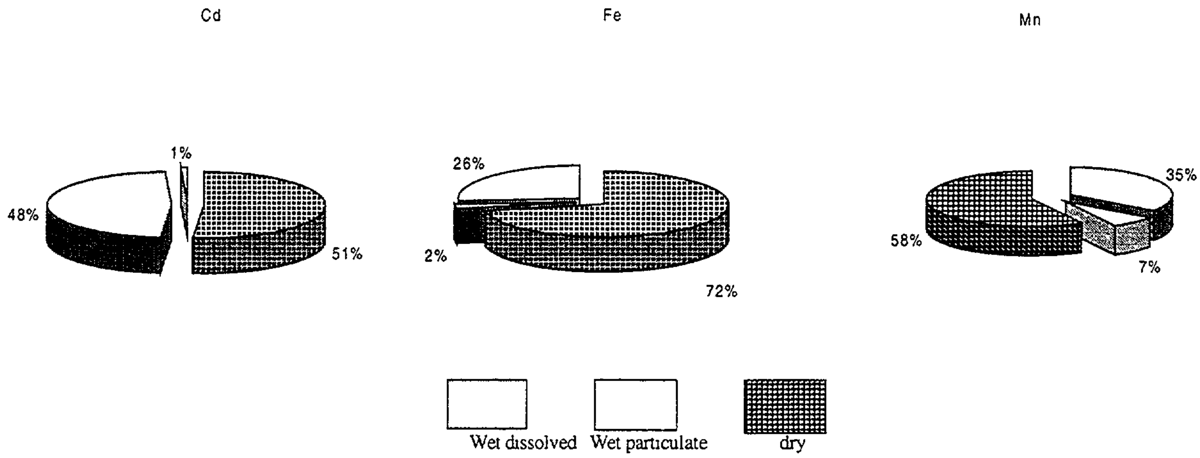

FIG. 1. Disolved and particulate fractions realative to various types of metals.

Coupled with concomitant sediment trap data, these results should bring worthy informations on exchange and transfer processes that occur in the water column (e.g., exchanges between dissolved material and suspended particles, mineralization, transfer of metals by biogenic or lithogenic particles). The potential fertilizing role of the atmosphere is also assessed, with the case of P, which probably regulates phytoplankton dynamics in the Mediterranean Sea [9, 10]. Phosphate concentration was measured in rainwaters from February 1997 to February 1998 at the Cap Ferrat sampling site. Soluble (reactive + complexed) and particulate P were distinguished. Total P concentrations exhibit a high temporal variability (0.05 to 4.3 µmol l^{-1}). Figure 2 shows the various P fluxes : for a total of 165 µmol m^{-2} y^{-1}, the dissolved and particulate inputs represent 95 and 70 µmol m^{-2} y^{-1} respectively. Anthropogenic emissions might be responsible for most of soluble (bioavailable) P.

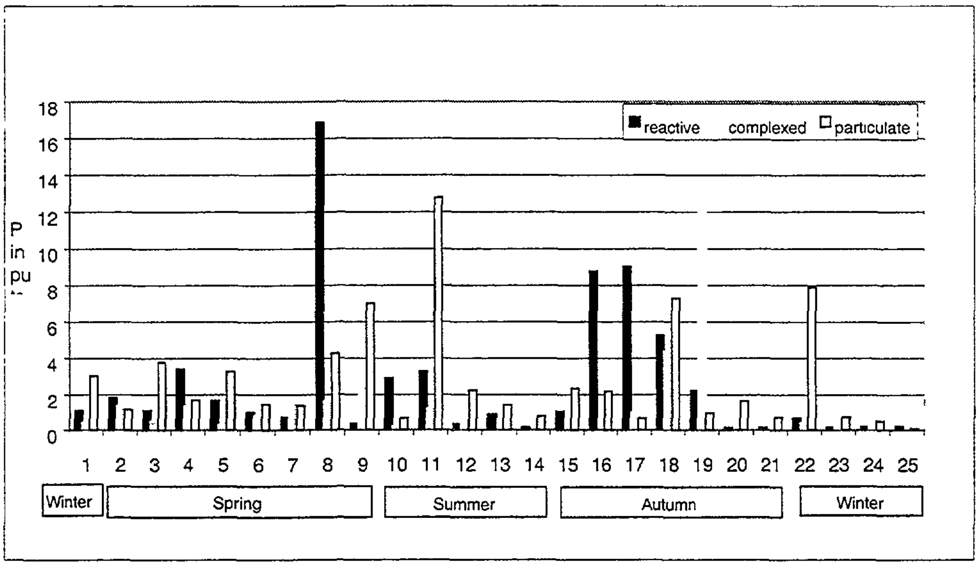

FIG. 2. Phosphate fluxes.

At a global scale, the atmosphere is a minor source of P (if compared with telluric inputs and marine vertical mixing). However, in oligotrophic conditions, it might be the only source of P to surface waters. For example, the rain event of June 19th 1997 (17 µmol reactive P m^{-2}) potentially induces a new production of 0.2 g C m^{-2}. This is a minimum value, which does not take into account the partial assimilation of complexed or particulate P.

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IAEA-SM-354/276P

ASSESSMENT OF THE RISK CREATED BY THE OBJECTS WITH SPENT NUCLEAR FUEL DUMPED IN THE KARA SEA AND INSTRUMENTAL POSSIBILITIES OF THE EARLY WARNING ABOUT RADIONUCLIDES DISCHARGES FROM THESE OBJECTS

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In the framework of the Project # 101B-96 of International Science and Technological Center (ISTC) in Moscow the detailed study of the peculiarities of the objects with spent nuclear fuel (SNF) and dumped in the Kara Sea between 1965 – 1981 was carried out. As a result a several most probable scenarios of corrosion of the objects protective barriers and radionuclides release were choosen. For these scenarios assessment of the risk of stochastic effects (carcinogenic and genetic) was made for population of Nenets autonomous district (AD) as an example. The doses are reaching maximum levels to the year 3000 and are about 0.1 – 0.5 nSv/year depending on diet. Main contribution is made by isotops of Pu – 239, 240 from Tsivolki Bay. More than 50% of the dose is due to fish consumption from Pechora Sea, 40% due to molluscs consumption. External irradiation and inhalation from those sources can not give more than several percents of the dose. Using maximum yearly dose rate (0.5 nSv/year) one will obtain the collective dose for the population of Nenets AD in the next 1000 years only 0.03 man.Sv, but even this value is much exaggerated.

The special probabilistic analysis of the one most probable scenario was made. The time of radionuclides discharge into sea water we will consider as the mean geometric assessment (GMt) of all possible release times. Standard geometric deviation of this value (GSDt) was choosen by the use of the worst and the best possible scenarios of release according to the formula to GSD assessment from selection < 5:

$$\ln GSDt = (\ln Maxt - \ln Mint)/2.3$$

where Maxt and Mint – times of releases according to best and worst scenarios. The values GSDt, 5%,50%,95% percentils for assessment of release times are given in the Table 1.

TABLE I. YEAR OF RADIONUCLIDES RELEASE FROM THE SITES OF DUMPING (50%), STANDARD GEOMETRIC DEVIATIONS (GSDT),YEARS CORRESPONDING TO 5% AND 95% PERCENTILS

	Actinides and fission products				*Activation products*			
Sites	*50%*	*GSDt*	*5%*	*95%*	*50%*	*GSDt*	*5%*	*95%*
Tsivolki Bay	2690	2.78	2310	4660	1967	-	-	-
Abrosimov Bay	2110	1.70	2060	2250	1965	-	-	-
Novaya Zemlya depression	3950	2.64	2940	8860	2070	1.94	2066	2330
Stepovoy Bay	6130	2.24	4270	13700	2280	2.45	2264	3710

Assessments of risk obtained here are showing that the level of hazard created by the dumped objects to population is extremely low. Nevertheless it could be much higher for individuals in close vicinity with the objects (for example, military personnel or polar explorers or tourists) at the time of enhanced release of radionuclides into sea water. Because of it the problem of early warning about radioactive discharge still exists. Highly sensitive gamma-spectrometer on the basis of NaI(Tl) crystal could be used as detection instrument. The system of detection consists of the sea module including gamma-spectrometer, radio transmitter and energy source connected by special cable. This system should perform its task for several years without servicing and replenishment. The most suitable sites for such systems are Tsivolky, Abrosimov and Stepovoy Bays. Similar systems may be used for marine radioactivity monitoring near the installations for treatment of liquid radioactive waste in Murmansk, Severodvinsk and Bolshoy Kamen, near SNF storage and disposal sites, near the sites of decommissioning operations with nuclear submarines and icebreakers.

IAEA-SM-354/277P

LONG RANGE TRANSPORT OF HYDROCARBONS IN THE SOUTHERN OCEAN

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The Southern Ocean is one of the more pristine areas in the world where the influence of the human activities remains still minor. However in the last decade, organo-chlorine compounds such as chlorinated hydrocarbons were detected in Antarctic atmosphere and hydrosphere [7]. The long-range transport by wind and water was responsible for the presence of these pollutants and it is likely that other anthropogenic compounds are being transported to the Antarctic Ocean. Several studies were conduced in the Antarctic marine environments in order to determine the extent of the hydrocarbon pollution. The sources of these compounds have been extensively reviewed by [2]. These authors concluded that hydrocarbon pollution is limited to few sources (shipwrecks, coastal research stations and shipping) and is very restricted in extent. The Antarctic marine environments contain hydrocarbons at low concentrations and therefore analyses require sensitive methods.

To date the available data are limited to coastal areas and Sub-Antarctic Islands. We report here the first results for hydrocarbon analyses of deep surface sediments collected in the Indian sector of the Southern Ocean. The samples were taken along a north-south transect ranging from 43° S to 55° S in the southwestern Crozet Basin. In order to identify these compounds and elucidate their origins, various techniques were used: gas chromatography and gas chromatography coupled with mass spectrometry; Accelerator Mass Spectrometry (Tandetron: mass spectrometer coupled with a Tandem accelerator allowing the measure of $^{14}C/^{12}C$ ratio).

Total hydrocarbon concentrations of uppermost sediments (0-1 cm) are in Table I.

TABLE I : HYDROCARBON COMPOSITION OF UPPERMOST SEDIMENTS (0-1 cm) COLLECTED IN THE SOUTHWESTERN CROZET BASIN (INDIAN SECTOR OF THE SOUTHERN OCEAN)

Cores	Latitude	Longitude	Total hydrocarbons (µg g^{-1} d.w.)	UCM (% of the total hydrocarbon concentration)
KTB05	55°02 S	71°48 E	33	76
KTB07	51°58 S	61°08 E	41	86
KTB13	50°01 S	58°00 E	102	95
KTB11	49°00 S	57°59 E	162	92
KTB16	48°00 S	56°00 E	104	92
KTB19	47°00 S	58°01 E	3	72
KTB21	45°58 S	55°59 E	3	69
KTB23	45°00 S	57°58 E	70	97
KTB26	43°58 S	55°58 E	2	56
KTB28	43°00 S	58°00 E	161	98

The concentrations are higher than those previously recorded in Antarctic sediments [2] and are for some samples typical of a petroleum input. Indeed organic-rich marine sediments may contain up to 100 µg g^{-1} dry wt of total aliphatic hydrocarbons, but higher concentrations are usually due to petroleum contamination [9]. Hydrocarbons are mainly composed of an unresolved complex mixture (UCM) in gas chromatography which represents 56 to 98 % of the total hydrocarbon concentrations. The UCM elutes in the range of n-C_{17} to n-C_{21} with a maximum in C_{18}-C_{19}.The presence of a UCM is usually considered as one of the more convincing indicators of petroleum contamination in water or sediment samples. However it has been also suggested that a UCM can result from recent bacterial degradation of organic matter [8,3] and/or weathering of ancient rocks [1]. The presence of petroleum biomarker hydrocarbons such as polycyclic compounds (hopanes, steranes, diasteranes, PAH) with a UCM allows to confirm or not the petroleum input. Distributions of these hydrocarbons are readily fingerprinted by the GC-MS technique even in small quantities. Few hopanes were detected in the uppermost sediments. The hopane, 17α(H), 21β(H) $C_{28}H_{48}$, dominates the distribution of the polycyclic hydrocarbons in all the samples. The α, β configuration of this compound suggests the presence of geologically "old" organic matter in the uppermost sediments. In order to test the hypothesis of a UCM associated with inputs of old organic matter in recent sediments, ^{14}C measurements of the hydrocarbon fraction were realised. Two samples were chosen for their higher hydrocarbon concentrations at the North and at the South of the study area. The data were obtained using a Tandetron. They confirm a fossil input into the hydrocarbon fraction and suggest a common source for the UCM in the western Crozet Basin. These unresolved compounds may be transported via the Antarctic Bottom Water which spreads from the South toward the North along the 56° E meridian [6]. The Weddell Sea contributes to the densest waters found in the western Crozet Basin. The Weddell Sea has been also defined as the most productive site of hydrocarbons in Antarctica [5] even though the poor quality of reservoirs has conduced these authors to suspect oil seeps. We may suppose that the Antarctic Bottom Water carries these compounds along to its path of spreading in the southwestern Crozet Basin. This hypothesis has been supported by the hydrocarbon analysis of samples collected in the Weddell Basin. The hydrocarbon composition presents characteristics similar to our hydrocarbon fractions: a UCM which elutes in the range of n-C_{17} to n-C_{21}, and α, β-hopanes as minor components [4].

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ALTERATIONS IN THE ORGANIC CARBON POOL RECORDED IN SEDIMENTS OF GUANABARA BAY, BRAZIL, A FERTILIZED TROPICAL ESTUARY

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As a consequence of anthropogenic impact in coastal areas, cycling of organic matter in these systems may be undergoing significant alterations, in response to the increased imbalance between natural (marine and terrestrial) and anthropogenic carbon. Assessment and comprehension of carbon fixation processes in coastal systems are matters of great concern because of its possible effects on atmospheric CO_2 excess derived from fossil fuel burning.

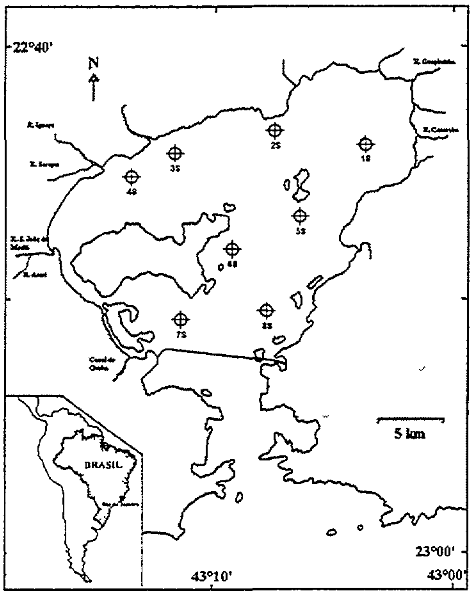
Guanabara Bay (Figure 1) is an estuary situated in the heart of Rio de Janeiro city. The bay receives 20 $m^3 s^{-1}$ of raw sewage derived from a population of about $5x10^6$ inhabitants living in the catchment area. In addition the bay receives waste waters from the second largest industrial district of Brazil as well as drainage from rural areas. Guanabara Bay is a specially interesting ecosystem to study alterations on carbon fixation due to the elevated primary productivity (average of 2 g C m^{-1} day^{-1})[1], high sedimentation rates (1-2 cm $year^{-1}$)[2] and high load of sewage derived nutrients (10^5 ton of P and 10^6 ton of N per year)[3].

We designed a core project in Guanabara Bay aimed at studying the possible anthropogenic impact on early diagenesis of sedimentary organic matter deposited in this system over the last century. The basic approach has been to look for the molecular, elemental (C, N e P) and isotopic compositions of organic matter in order to obtain the necessary information. The present work presents data on C, P and isotopic composition of organic matter, as well as the results of polyaromatic hydrocarbons, sedimentation rates and humic acids so far obtained for cores collected at several stations in the bay.

Sediment cores (each with *ca* 60-70 cm length) , collected from eight stations in the bay, were first sliced under nitrogen atmosphere and then freeze-dried. Elemental analyses were performed in a Perkin Elmer CHN analyzer after removal of inorganic carbon with hydrochloric acid; organic phosphorus was obtained by difference between total and inorganic phosphorus; $\delta^{13}C$ in the organic matter was determined in a Finnigan MAT 252 mass spectrometer, using PDB as reference; humic acids were extracted with NaOH, purified and freeze-dried; for determination of polyaromatic hydrocarbons, we used Soxhlet extraction followed by quantification by GC/FID. Sedimentation rates were determined using Pb-210.

Results for the several measured properties are in the range of: 2.30-6.60% for organic carbon; -21.12 to - 32.99‰ for $\delta^{13}C_{oc}$; 1.57-12.35% for humic acids in organic matter; 1.83-16.72 $\mu mol\ g^{-1}$ for organic phosphorus. The variations of P and C along the sediment core are related to changes in sedimentation rate rather than to preferential remobilization[4]. The plot of C/P (mean of 583.5) versus $\delta^{13}C_{oc}$ (mean of –23.04 ‰) allows the grouping of samples with different depositional patterns (see Figure 2): group 1 (samples in station 5s) is dominated by marine organic matter; group 2 is dominated by terrestrial organic matter (high C/P and low $\delta^{13}C_{oc}$) deposited 30-40 years ago; group 3 (samples from station 6s) is influenced by increasing flux of C and P and terrestrial organic matter; group 4 (deep samples from 6s) may be influenced by methanogenesis. As observed in previous work large changes in the carbon pool are mainly restricted to the upper layers of sediment. Sediments, in general, have low humic content and possibly the organic carbon pool is mainly composed of humine. This observation may explain the rather constant carbon accumulation in periods of similar sedimentation rates. Measurements of sulfate reduction activity[5] already suggested the presence of refractory organic matter, probably derived from intense microbial respiration rates in the water column and surface sediment.

Besides an increase in carbon sedimentation rate, specially over the last 50 years, we observed a dramatic chance in composition of organic matter. Of special environmental concern are the PAHs whose total concentration varied from 100-250 ng g^{-1} in the beginning of the 20th century to 12,000 ng g^{-1} in the present. In the past PAHs were derived from biomass combustion while in recent sediment samples there are major contributions of petrogenic PAHs.



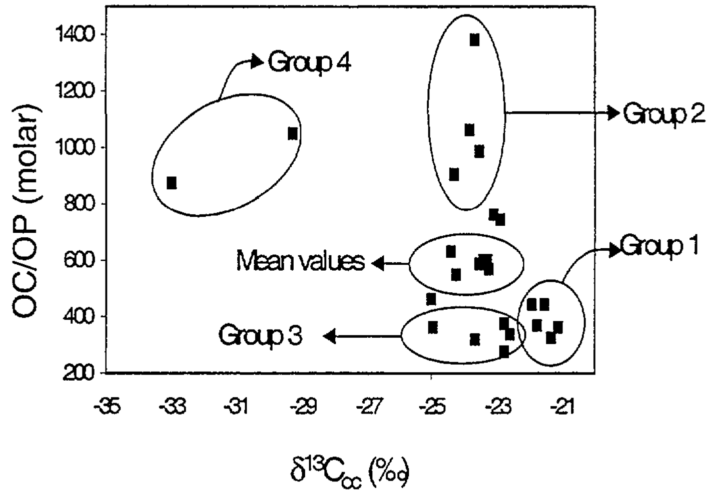


FIG. 2. Plot of C/P ratio versus $\delta^{13}C$ of organic matter for stations 3s, 4s, 5s and 6s.

FIG. 1. Localization of Gauanbara Bay and samplimg points.

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MONITORING AND MEASUREMENTS OF RADIOACTIVITY AROUND THE VALLEY OF MADJERDAH RIVER IN TUNISIA

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This paper discusses the efforts being made by the National Center for Nuclear Sciences and Technologies of Tunisia in cooperation with the Faculti des Sciences de Tunis to monitor the environmental radioactivity in soil and water around the valley of Madjerda. Preliminary results of the radioactivity measured in soil, water and grass samples from the northern region of Tunisia are given. Measurements are being taken on a continuous basis in order to accumulate a useful database on natural and possible man-made radionuclides found in the area. This information is necessary in order to monitor future nuclear activities and to have a baseline for comparison purposes.

The results showed normal radioactivity values for the natural radionuclides of the uranium series (form 10 to 25 Bq/kg for U-238) and for thorium series (from 11 to 30 Bq/kg for Th-232) and for potassium (from 30 to 520 Bq/kg). Traces of Cs-137 are detected and the activity varied from 0 to 12 in April 1998 and from 0 to 23 in August 1998. This phenomena is to be investigated more carefully. Water and grass samples gave values that were near the lower limit of detection.

The Madjerda river is the only major source of potable water in Tunisia. For this reason, we decided to conduct a campaign to measure the background radioactivity levels around this river. We focused attention on the Site of Sidi Thabet, 20 km north of Tunis, which is chosen to be the techno-pole for peaceful nuclear activities and development in Tunisia. These activities require strict monitoring programs of any possible radionuclide release to the environment. Hence, background information on natural radioactivity is mandatory in order to have reference values against which any eventual contamination can be checked.

Previous studies concerning radiation levels in Tunisia did not show major radioactivity levels of artificial gamma-emitting nuclides (such as Cs-137). On the other hand, it is reported that an important contribution to the overall radiation field is due mainly to the uranium and thorium series and potassium 40, which is a direct consequence of the igneous nature of the Tunisian geology and its large phosphate reserves.

This study in particular, focuses on the gamma emitting radionuclides that contribute to the natural radiation around the valley of the Madjerda river in general, and around the site of Sidi Thabet, an area of 60 000 m2, in particular.

Sampling is conducted according to the IAEA guideleines [Ref. 1]. The gamma spectrometry setup consists of a vertical high purity lithium-drifted germanium (Ge(Li)) detector with sealed preamplifier, a bias high voltage supply, a linear amplifier, a detector shield made of 5 cm thick lead bricks lined with a 1 cm thick steel tube for X-rays degradation, a multichannel analyzer (MCA) with a 8K channels connected to a PC and a spectroscopy analysis software (GammaVision, Ortec, EG&E).

The detector is GC1020 Canberra-made closed-end coaxial (P-type) with crystal diameter of 55.5 mm and length 40 mm and having a resolution of 0.86 keV at 122 keV and 1.81 keV at 1332 keV and a relative efficiency equal to 34.1 and a Peak / Compton ratio of 60.6 / 1.

Soil activity in three different sites in Sidi Thabet for the months of April and August 1998 is given numerically in Table 1. The activity values for the month of August is double what it was in April for the same year (1998). The origin of this increase, which is about the same for both natural and artificial radionuclides, could not be determined at this time. More measurements are needed for this purpose. The presence of the cosmogenic Be-7 is attributed to the collection method (5 cm sampling depth). Usually, Be-7 forms a thin layer on the surface of the soil and does not migrate to deeper levels.

Table II gives detailed soil activity in Sidi Thabet for the month of August 1998. The average activity of Cs-137 is 8.7 Bq/kg. The maximum level found is 23 Bq/kg. Some sites did not have any level of Cs-137. This wide variations in the Cs-137 levels could be attributed to differences in altitude, the nature of soil and to the effects of soil erosion. The elevation of the site of Sidi Thabet varies from 20 to 80 m above sea level. In addition, several water ways exist on the site. The presence of human activities (construction of the future site) in the low elevation sites contribute also to the reduction of the Cs-137 level.

TABLE I. SOIL ACTIVITY IN SIDI THABET FOR THE MONTHS OF APRIL AND AUGUST 1998

SITE 05	A: 30/04/98		B: 18/08/98		Diff %
	Bq/kg	+/-	Bq/kg	+/-	(B-A)/B
Cs-137	12.3	0.46	22.7	0.39	46.04
Be-7	0.0	0.00	0.0	0.00	0.00
K-40	142.6	7.10	239.3	5.57	40.39
U-238	5.9	0.46	12.5	0.47	52.97
Th-232	9.3	1.28	16.0	1.13	42.23
SITE 07	30/04/98		02/09/98		Diff %
	Bq/kg	+/-	Bq/kg	+/-	
Cs-137	1.6	0.18	18.2	0.4	91.3
Be-7	5.9	0.4	8.8	1.23	32.46
K-40	104.9	5.6	293.3	7.15	64.25
U-238	5.9	0.4	15.6	0.53	62.04
Th-232	7.4	0.84	18.5	1.1	59.83
SITE 19	30/04/98		18/08/98		Diff %
	Bq/kg	+/-	Bq/kg	+/-	
Cs-137	3.7	0.25	2.79	0.35	-33.69
Be-7	0.0	0.00	10.05	1.76	100
K-40	173.1	6.57	345.1	7.71	49.822
U-238	9.4	0.49	21.51	0.68	56.346
Th-232	8.9	0.92	22.57	1.87	60.39

TABLE II. SOIL ACTIVITY (Bq/kg) IN SIDI THABET FOR THE MONTH AUGUST 1998

	Cs-137	+/-	Be-7	+/-	K-40	+/-	U-238	+/-	Th-232	+/-	Sampling date
site											
2	10.9	0.31	0.0	0.00	252.1	5.97	15.9	0.53	16.8	1.17	18/08/98
5	22.7	0.39	0.0	0.00	239.3	5.57	12.5	0.47	16.0	1.13	18/08/98
7	18.2	0.40	8.8	1.23	293.3	7.15	15.6	0.53	18.5	1.1	02/09/98
8	0.0	0.00	3.5	0.70	330.5	6.71	20.0	0.54	22.8	1.26	18/08/98
11	0.7	0.16	4.5	0.95	228.0	5.35	14.9	0.45	17.1	0.89	02/09/98
13	17.5	0.49	2.4	0.64	272.0	6.34	18.9	0.79	19.8	1.06	18/08/98
14	10.9	0.47	43.7	2.05	324.5	7.67	17.1	0.62	21.9	1.17	18/08/98
17	3.1	0.46	7.1	1.44	337.0	8.88	18.8	0.68	21.3	1.32	02/09/98
19	2.8	0.35	10.1	1.76	345.1	7.71	21.5	0.68	22.6	1.87	02/09/98
20	8.4	0.57	0.0	0.00	160.7	7.9	14.5	0.88	12.5	1.80	18/08/98
24	1.6	0.20	1.4	0.54	306.5	6.01	17.8	0.48	20.6	1.10	02/09/98
26	7.8	0.32	12.3	1.4	321.2	7.05	17.4	0.72	24.6	1.53	02/09/98
Ave.	8.7		7.8		284.2		17.1		19.5		
Max	22.7		43.7		245.1		21.5		24.6		
Min.	0.0		0.0		160.7		12.5		12.5		

The variations in the B-7 activities (from 0 to 45 Bq/kg) is attributed to the method of sampling. Inconsistency in the method of collection and especially the sampling depth could result in wide variations in the presence of Be-7. Activity values for K-40 varied from 160 Bq/kg to 350 Bq/kg. The activity values for both U-238 and Th-232 varied between 10 and 25 Bq/kg.

Table III gives values of soil activity in different regions around the valley of Madjerda. Cs-137 activity varies from 0 to a maximum of 10 Bq/kg, wheras, for Be-7, activity was measured only in two sites and reached 7 Bq/kg. Potassium 40 activity varied from 30 to 520 Bq/kg. The lower values are due to the sandy nature of the soil. The activity values for both U-238 and Th-232 varied between 3 and 30 Bq/kg.

Table IV gives the average values of the radioactivity measured for different regions in the south of Tunisia and for different soil characteristics [Ref.4] and values measured for Sidi Thabet, north of Tunisia.

TABLE III: SOIL ACTIVITY AROUND THE VALLEY OF MADJERDA FOR THE MONTHS JULY AND SEPTEMBER 1998

site	Cs-137	+/-	Be-7	+/-	K-40	+/-	U-238	+/-	Th-232	+/-	Sampling date
Tunis	0.3	0.07	1.1	0.45	28.6	3.0	20.2	0.45	12.2	0.66	07/29/98
Ichkel	19.7	0.56	0.0	0.0	517.8	14.64	26.5	1.64	28.5	2.64	07/17/98
Ichkel	23.2	0.42	7.1	1.91	367.4	7.05	26.4	1.21	26.4	5.3	07/17/98
Joumine	3.9	0.23	7.5	1.55	122.9	6.21	11.4	0.75	11.7	1.09	07/17/98
Ghazala	0.0	0.0	0.0	0.0	44.8	3.54	8.9	0.34	5.3	0.73	07/17/98
Nefsa 1	5.0	0.3	0.0	0.0	292.5	7.61	22.7	0.61	30.0	1.35	09/15/98
Nefsa 2	0.4	0.12	0.0	0.0	3.8	2.92	3.4	0.25	1.8	0.52	09/15/98

TABLE IV. SOIL ACTIVITY IN DIFFERENT REGIONS IN TUNISIA

	Ra-226	Th-232	U-238	K-40	Cs-137
Clay					
near	46 (32-74)	19(12-30)	51(32-130)	277(100-470)	<3
away	22 (7-80	15(6-30)	22(7-96)	261(122-420)	<3
Limestone					
Near	31(20-50)	23(15-30)	40(28-63)	13 (5- 23)	<3
Away	15(7-25)	12(6-23)	17 (3-39)	69 (7-280)	<3
Sand					
Near	10(7-14)	11(8-13)	10(7-12)	171 (116-250)	<3
Away	14 (7-26)	11 (7-22)	12(6-20)	166 (100-230)	<3
Sidi Thabet	34(22-61)	19.5(12-25)	17(12-22)	284(160-350)	8.7(0-23)

Regions that are near phosphate deposits are indicated with the word Near, and those for regions far away for phosphate regions are indicated with the word (Away). The different measuring locations do not vary much in composition and hence in natural radionuclide concentration. Activity values for U-238, Th-232 and K-40 were similar for regions in the south that are away from phosphate deposits and regions in Sidi Thabet. Radioactivity varies from 12 to 22 Bq/kg for U-238, from 12 to 25 Bq/kg for Th-232 and from 160 to 350 Bq/kg for K-40. An exception to this is the detection of Be-7 and of Cs-137. On two occasions we measured values around 20 Bq/kg for Cs-137. The activity for Be-7 varied between 0 and 43 Bq/kg. These measurements indicate that the activity values for Cs-137 are higher in the north of Tunisia (Sidi Thabet) as compared to the south, where the activity was always below 3 Bq/kg [Ref. 4]. Additional measurements are being carried out in order to verify this happening. The installation of a newly acquired professional lead shield in the near future will allow us to refine these measurements.

We have presented preliminary results for the radioactivity in the soil around the Madjerda river and around the site of Sidi Thabet, the future site of the nuclear activities in Tunisia. We have noted an important presence of the natural radionuclides of U-238, Th-232 and K-40 and their daughter products. However, water and grass samples showed radioactivity values below our LLD and future measurements of larger samples are needed for any meaningful results. We also observed wide variations in the presence of Cs-137, an artificial radionuclide, and an occasional presence of Be-7. More measurements are needed to investigate further the presence of both Cs-137 and Be-7.

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Pb, Cd, Cu AND Zn BIOGEOCHEMICAL BEHAVIOUR AND BIOLOGICAL TRANSFER PROCESSES IN THE NORTHWESTERN MEDITERRANEAN

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Cd, Pb, Cu and Zn concentrations were determined in planktonic organisms (Salps, copepods), their associated faecal pellets and in particles collected at 200 and 2000 m depth in sediment traps moored in the Ligurian Sea (1). Al and P were also measured and taken as tracers of lithogenic and biogenic components, respectively. The aim of this work was to determine the fluxes of trace metals in the Ligurian Sea and their variations with depth, and to to assess the biogeochemical behaviour of elements having, for some of them, an anthropogenic origin, by the study of biologically-mediated uptake and removal processes (2).

The total particulate mass flux decreases with depth, from 180 ± 90 mg m^{-2} d^{-1} at 200 m to 130 mg m^{-2} d^{-1} at 2000 m. A similar decrease with depth is observed for Cd, Pb, Zn and P particulate concentrations, suggesting that these elements are partially carried by biogenic particles that decompose during settling. Conversely, the increase with depth of Al and Cu concentrations and fluxes seems consistent with a refractory behaviour of elements associated to lithogenic aluminosilicate particles « pakaged » in the biogenic one by the biological activity (3).

The apparent residence time of elements in surface and deep waters is established from the average dissolved concentrations in the Ligurian Sea (4) and the particulate fluxes observed at 200 and 2000 m depth, respectively. The longest residence time is found for Cd (20 and 80 years for surface and deep waters, respectively). This element exhibits a strong decrease of flux with depth consistent with a rapid recycling in surface waters and a transport by labile biogenic particles easily mineralized when settling. The very short residence time observed for Pb (6 months in surface waters), indicates an efficient transfer of this metal, Which has an anthropogenic origin and enters the sea surface by the atmospheric pathway.

An enrichment factor (EF) calculated as the metal/P ratios in the particulate materials normalized to the same ratios in seawater is used to assess the degree to which each element is involved in the dissolved-particulate exchanges (5). Globally, for all metals EF is lower than 1 in planktonic species and up to the unity in detritical particles : metals are less mobilized than P in living organisms that excret the non assimiled metals in faecal pellets, known to be a significant contributor to the downward particulate flux (6). A ratio > 10 for some elements of continental origin (natural, Al, or anthropogenic, Pb) in settling particles reflects the presence of abiotic particles packaged with the biotic ones. The implication of biogenic particles as carriers increases with the residence time of elements (i.e. decreases with the settling velocity of associated particles). Elements (e.g., Al, Pb) mainly carried by lithogenic particles are poorly mineralized during their downward transfer and their biogeochemical cycle is only controlled by the temporal variability of the biological activity therefore. On the contrary, the mineralization of elements (e.g., Cd) mainly carried by biotic particles is significant and they are recycled in surface waters, which leads to the apparent paradox that their biogeochemical cycle in the western Mediterranean Sea is regulated by hydrological processes. For the case of Cu, EF is > 1 in faecal pellets, becomes slightly < 1 at 200 m depth and > 1 again at 2000 m depth. This presumably indicates that Cu is transported by two distinct types of particles : there is a biotic component, which is rapidly mineralized, and a lithogenic one, which leads to a relatively high EF value in deep waters.

Acknowledgements

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THE DYFAMED TIME-SERIES STATION : A REFERENCE SITE FOR ENVIRONMENTAL STUDIES IN THE NORTH WESTERN MEDITERRANEAN SEA

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The observation site is located in the central part of the Ligurian sea, at about 50 Km off Nice, on the Nice Corsica transect. The Ligurian sea is characterised by three different areas [1,7)]. The coastal area is submitted to inputs from coast and from the liguro-provencal current. The frontal zone is delimited by the ligurian current and the central area . This frontal zone isolates the central part of the basin where is located the DYFAMED site. In this central area, the primary production is dependent on inputs of nutrients from deeper waters but also, for a badly evaluated part, on atmospheric inputs of nitrogen and some trace metals particularly during summer [5]. Since 1987, data have been collected on the time series station, in the frame of the Jgofs-France program. Then, the scientific observation service has been officially created by INSU/CNRS in 1995 [6]. It is composed of 3 elements :

- Permanent mooring ; sediment trap (traps at 200 and 1000 m depth) and current meters ; data from 1988
- Monthly cruises for hydrological and biogeochemical data (water column and sediment) beginning in 1991
- Atmospheric inputs from Cap Ferrat station (wet and dry deposition) ; data since 1989.

Data are available in the Jgofs-France data base : http://www.obs-vlfr.fr/jgofs/html/bdjgofs.html

Seasonal changes in the temperature variations for the surface layer indicate that water temperature is homogeneous from surface to depth (#13°C) from December to the end of march. From the beginning of April, there is a gradual increase of the surface temperature. The temperature reaches 26 °C in July/August. This reinforcement of the thermal stratification is maximum from July to October, when the destratification begins.

Nutrient concentrations follow the general pattern of thermal stratification. Nitrates are at undetectable concentrations from end April to November in the superficial layer after winter mixing. The deepness of the nitrates-impoverished layer increases from April to October, following the increasing depth of the warmed layer.

The chlorophyll a maximum occurs at increasing depth from April to October, following approximately the 13.5°C isotherm or nitracline. The phytoplankton community structures can be described by the evolution of specific pigments [3,2]. Fucoxanthin, which is the specific pigment of diatoms, is particularly abundant in the beginning of blooming period as a result of the opportunistic behaviour of these species. The bloom period is characterised by the abundance of nanoplankton : flagellates (19'Hexanoyloxyfucoxanthin as example) which are the main constituents of the phytoplankton biomass all along the year in the Mediterranean sea. The oligotrophic period from July to November is characterised by the presence of picoplankton : prochlorophytes (Divinyl chl a, and cyanobacteria (zeaxanthin), which are the typical species of the oligotrophic systems.

Since 1997 transects from Nice to Corsica have been undertaken in order to confirm the representativity of the DYFAMED site with respect to the central zone of the Ligurian sea. Stations have been sampled every 5 nautical miles along the transect in May, February and September, i.e. during the three characteristic regimes encountered along the year -namely spring mesotrophy, summer/fall oligotrophy and winter mixing- will be sampled. The results confirm the contrast between lateral and central zone which was been already observed by[1] and the independence of the observation site from direct coastal inputs.

In order to attain the scale of some biogeochemical processes, it is clear that continuous measurements for selected relevant parameters is necessary. This is the case for small-scale processes which have been shown to deeply influence higher scale variations. This is true for meteorological forcings which cannot be adequately described neither from coastal observations nor from models, but also for trophic dynamics (Vidussi et al. Submitted) and for particulate vertical flux of matter [8].

In the near future (spring 99) a meteorological buoy will be moored at the DYFAMED site. A project is also developed (Boussole project, D. Antoine) for the development of a buoy support of optical sensors in relation to satellital measurements. Since some biogeochemical variables (e.g. vegetal matter, non-vegetal, detritic, some phytoplanktonic groups...) possess specific optical signatures (absorption, diffusion and fluorescence), they are potentially measurable via optical sensors. The first data on vertical profiles at DYFAMED site were obtained using the AC9 (absorption ant attenuation at 9 wavelength). The vegetal biomass is well described by absorption at 676 nm, and the particulate charge by attenuation at 555 nm. The proportion between vegetal and non vegetal matter is estimated by the ratio of absorption at 440 versus 410 nm.

Acknowledgements

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MONITORING OF RADIONUCLIDES IN THE AIR OF MONACO DURING 1997-1998

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IAEA-MEL has been carried out monitoring of radionuclides in the air of Monaco for several years. Several natural (cosmogenic, radiogenic and primordial) and anthropogenic radionuclides are found in the atmosphere. The measurement of these radionuclides in the atmosphere is helping to study their temporal variations and to estimate their deposition rates to oceans and to seas. We report here concentrations of some radionuclides in air of Monaco during 1997-1998.

The air filtering system used is Sierra-Anderson (type 305-200 H-1). This system is installed on the roof of the Musée Oceanographique (Monaco, 43°50'N, 7°30'E). The sampling is done monthly (except for June 1998 when we registered ^{137}Cs signal and the sampling was done weekly). 1000-4000 m^3 of air is collected in glass fibre filters with a flow rate of 1.4 m^3 per minute. The rainwater (or dry fallout) collector system is installed in the roof of the new laboratory (Quais Antoine 1er, Monaco). Its surface dimension is 2x2 m^2. If it was raining during the month, 20 liters of representative rainwater sample is taken after homogenization for the analysis. If it was not raining, the dry fallout sample is collected by cleaning the surface of the collector system with acidified distilled water. The samples are concentrated by evaporation and counted by gamma-spectrometry (150% efficiency HPGe detector).

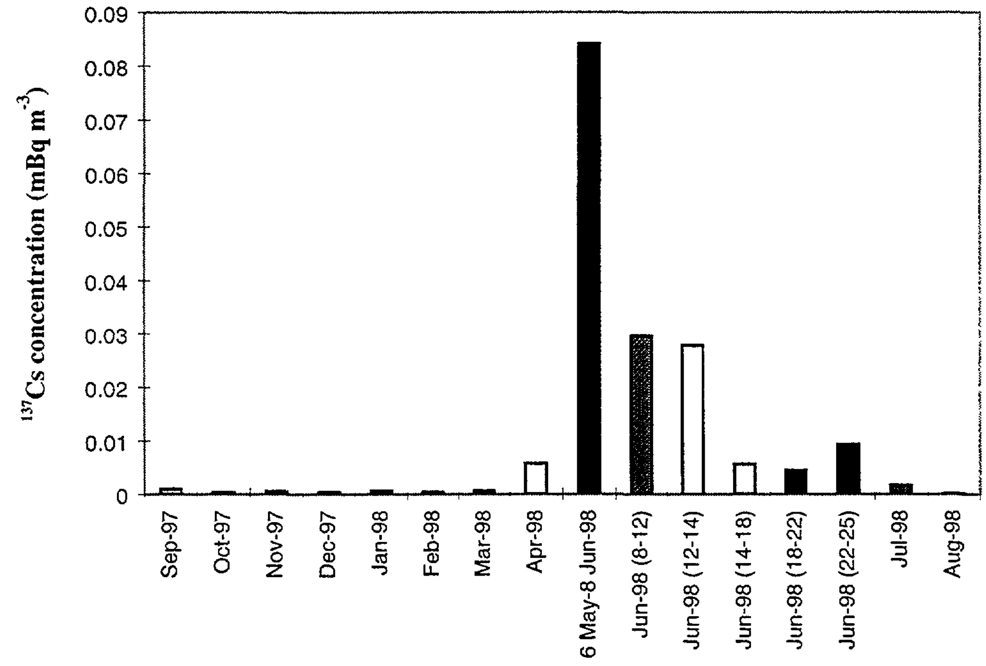

FIG.1. ^{137}Cs concentration in air collected in Monaco.

A clear ^{137}Cs signal was observed during May-June 1998 in both air filter (Fig.1) and rainwater samples (Fig.2). This radionuclide was produced in an accident during iron melting in the south of Spain (Algeciras). The estimated ^{137}Cs concentration in the radioactive "cloud" over the Monaco at the end of May and the beginning of June is 2.7 mBq m^{-3}. This value is in accordance with the one registered (2.48 mBq m^{-3}) in La Seyne sur Mer (Toulon, France) on aerosol samples from May 25th to June 2nd [1]. The ^{137}Cs concentration decreased progressively for the weeks after in June and a normal value (as before the accident) was found in August 1998.

Concerning the cosmogenic ^{7}Be radionuclide, we observe a monthly variation of ^{7}Be concentration both in air and in rainwater (data not shown here). The highest values in air were observed for the months of March, May and June, which correspond with the ones found in rainwater for these months. ^{7}Be data show typical variations throughout the year due to special stratospheric-tropospheric mixing [2].

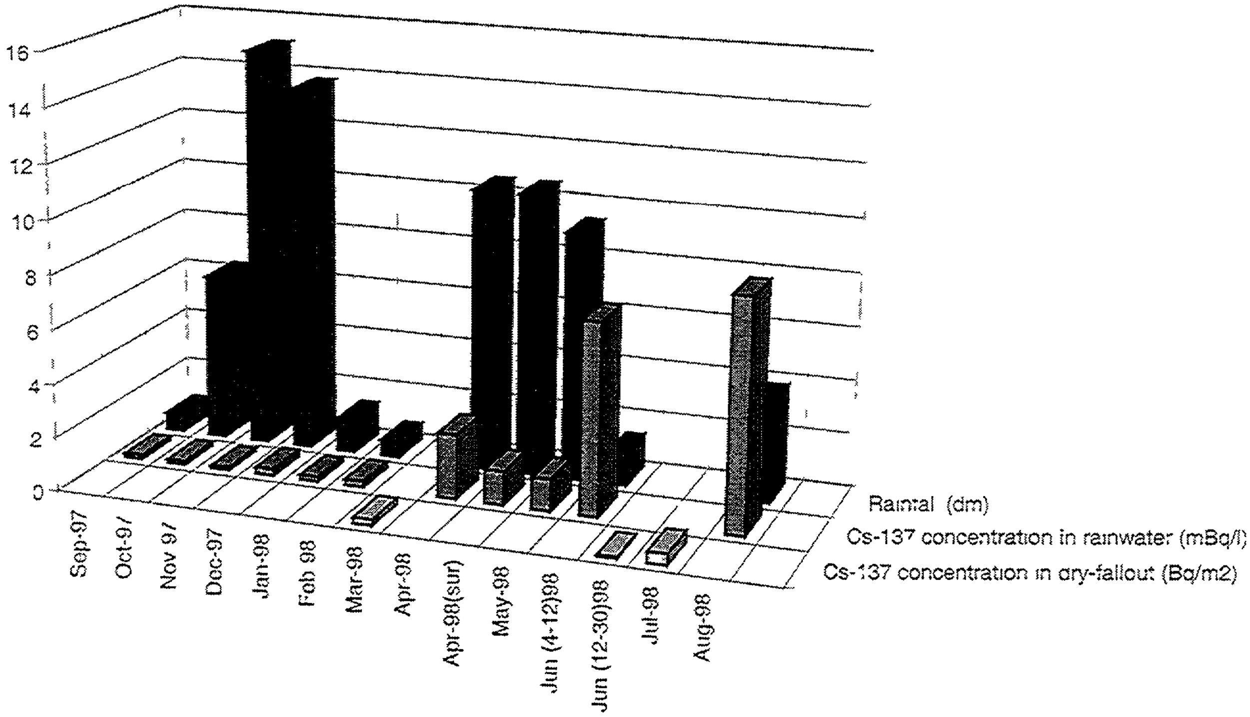

FIG.2. ^{137}Cs concentration in rainwater and dry-fallout collected in Monaco.

Acknowledgements

The authors would like to thank F. Avaullee for his help with installing the air filter and rainwater collector systems.

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ASSESSMENT OF ALGECIRAS FALLOUT DISTRIBUTION OVER THE SOUTHERN PART OF FRANCE

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The Nuclear Safety and Protection Institute operates a Permanent Observatory of Radioactivity Levels in the environment. This network concerns the levels of natural and artificial radionuclides of the atmosphere, the terrestrial and the marine environmental components of the French territory.

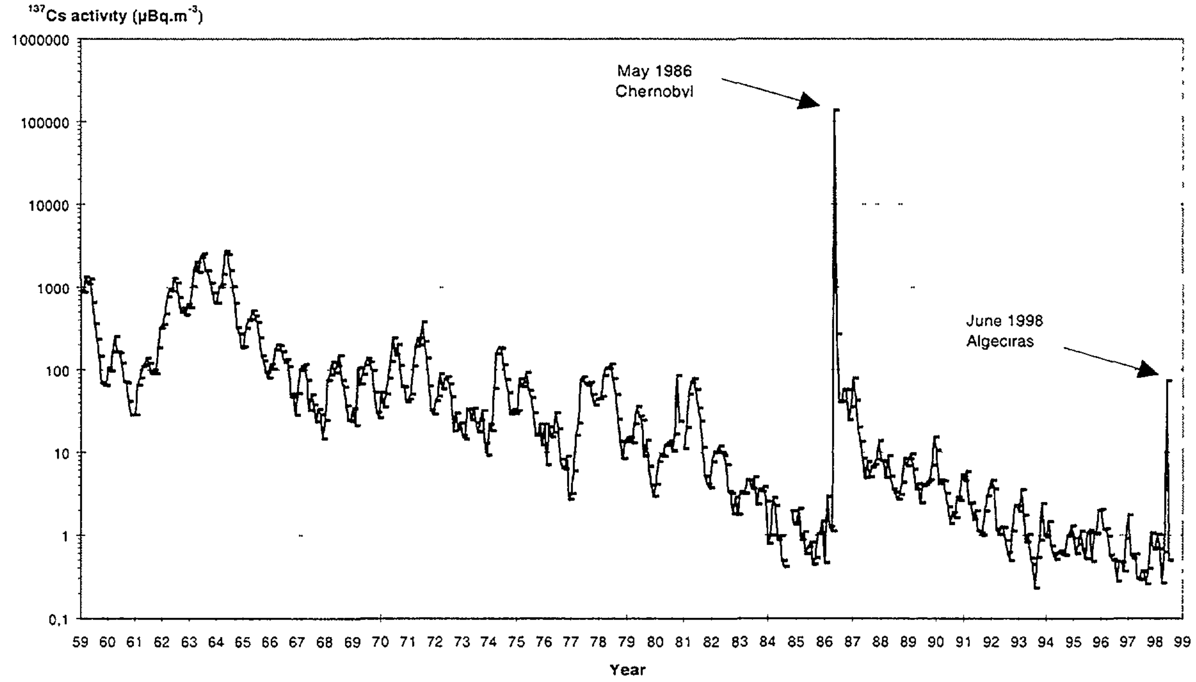

FIG. 1. Temporal evolution of ^{137}Cs (monthly average of the french territory stations) in aerosol samples in France from 1959 to 1998.

A substantial increase in ^{137}Cs levels in aerosols appeared in June 1998 over the southern part of Europe. The monthly average ^{137}Cs concentration for France increase from 0.7 µBq.m^{-3}, for the first five months, to 73.9 µBq.m^{-3} in June. This signal was due to the ^{137}Cs released from a source accidentally melted and incinerated between May 29th and May 30th in a steel mill in Algeciras, situated in the South of Spain. A maximum value of 2,480 µBq.m^{-3} was registered in La Seyne sur Mer on aerosols sampled from May 25th to June 2nd that decreased to 195 ± 10 µBq.m^{-3} for the period June 2nd - June 5th. The concentrations, measured 2 weeks later in the different aerosol samples collected at the 6 stations of Flers, Orsay, Charleville-Mézières, Bordeaux, Dijon and La Seyne sur Mer, were back to levels observed previously, about 1 µBq.m^{-3}.

From January to May 1998, the average ^{137}Cs activity in rain water collected all over the french territory was 0.12 Bq.m^{-3}, with a maximum of 1.7 Bq.m^{-3} observed in May. Following the Algeciras incident an increase was observed in the June rain water at Charleville-Mézières, Bordeaux and Orsay, respectively 13.7 ± 1.3 Bq.m^{-3}, 5.1 ± 1.5 Bq.m^{-3}, 2.2 ± 0.4 Bq.m^{-3} (May 29th - June 12th). At the beginning of June, no precipitation was collected at La Seyne sur mer, preventing the detection of ^{137}Cs, as well as its « wet » deposition on the ground of this site.

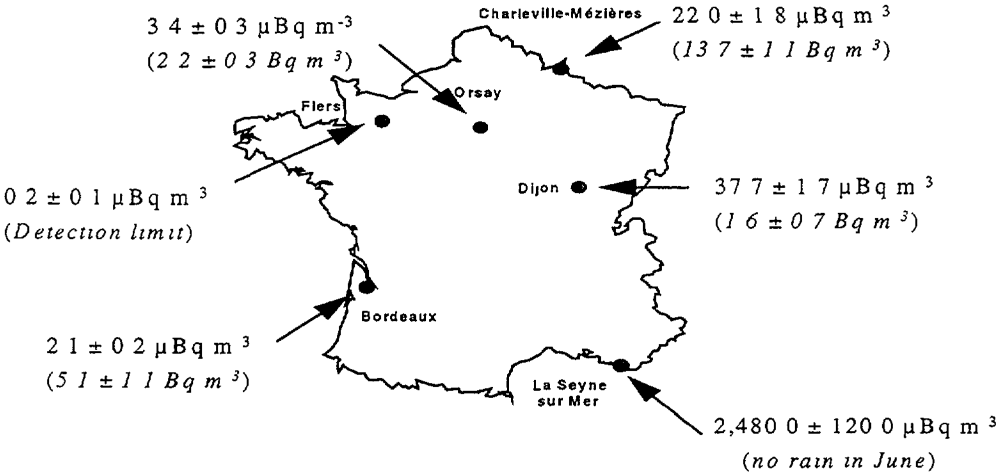

FIG. 2. ^{137}Cs activity in aerosols (µBq.m ^{3}) and rain water (Bq.m ^{3}) - first day of June

In order to evaluate the distribution of this input, different environmental samples were collected in June along the Mediterranean coastal zone that might have received most of the potential fallout. Bio-indicators such as pine needles, thyme, mosses, algae and mussels were sampled. ^{137}Cs concentrations in these different sentinel organisms have shown no signifiant increase since they were in the same range of those regularly observed in this area

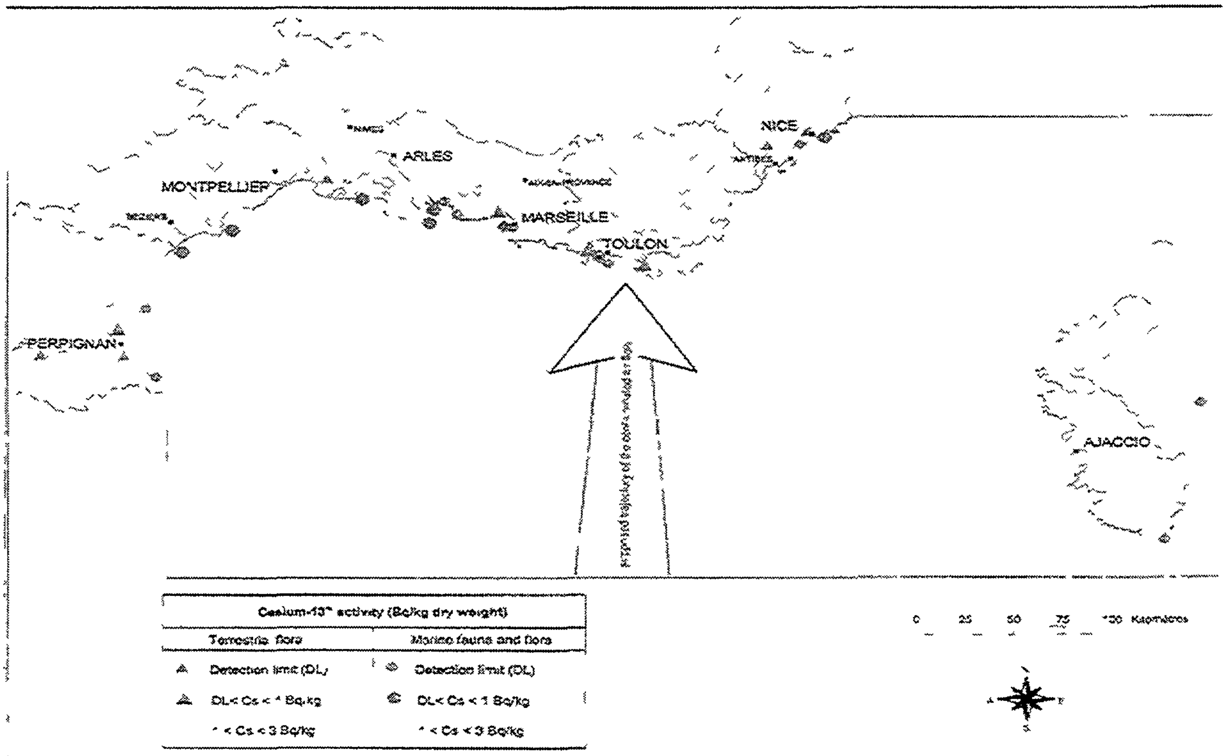

FIG. 3. ^{137}Cs activity in bio-indicators

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MARINE RADIOACTIVITY MEASUREMENTS WITH LIQUID SCINTILLATION SPECTROMETERS

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Liquid Scintillation Spectrometry (LSS) has now become the most widespread method for quantitative analytical measurement of low levels of β-emitting radionuclides like ^{3}H and ^{14}C. The high efficiency resulting from the latest development in LSS makes this technique not only appropriate but also enables direct measurement in environmental samples without excessive preparation. The introduction of several new cocktails based on solvents with a high flashpoint containing surfactants and having a high degree of aqueous sample compatibility has also contributed to the simplification of procedures.

Of all the chemical forms of tritium, HTO is the most relevant because firstly, it is the most radiotoxic and secondly, it is the oxidation product of the other tritium gaseous forms. The most common way to recover tritiated water is by distillation. To avoid isotopic fractionation, the distillation must go to complete dryness taking care to prevent contamination resulting from degraded volatile products that might be present in the sample.

When measuring very low activities, care must be also taken to prevent possible contamination from water vapours present in the air. After mixing with the scintillator in low-background Teflon®-copper vials (Wallac), the cocktail is placed in the spectrometer (Quantulus 1220). Based on the procedure described the previous publication [1], three commercial scintillators, Packard Insta-Gel® Plus, Packard Ultima Gold™ and Wallac OptiPhase TriSafe™ were studied. Figure 1 compares minimum measurable activity (MMA) [1] obtained with these scintillators. The Packard Insta-Gel® Plus gives the best parameters as it exhibits high water compatibility and has the lowest minimum measurable activity.

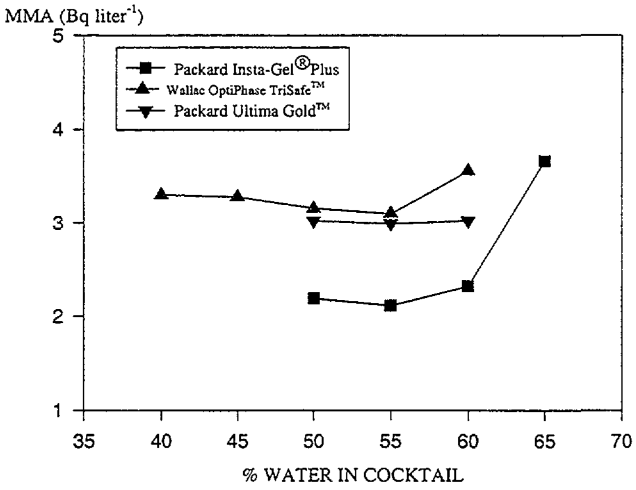

FIG. 1. MMA vs. admixture of water in Insta-Gel® Plus, OptiPhase TriSafe™ and Ultima Gold™ cocktails (relative standard uncertainty 10% and 48 hrs counting)

In July 1996, a marine sampling expedition took place at Mururoa and Fangataufa Atolls within the framework of an IAEA project [2]. Several water samples were taken at different sites and analysed for ^{3}H and ^{90}Sr as well as for other anthropogenic radionuclides. Another sampling expedition to the atolls took place in 1997 when samples of water from underground cavities formed after nuclear bomb explosions as well as from underground monitoring wells were collected [3].

Similarly, as for surface samples, the radionuclides analysed were ^{3}H, ^{90}Sr, ^{137}Cs, ^{241}Am and plutonium isotopes.

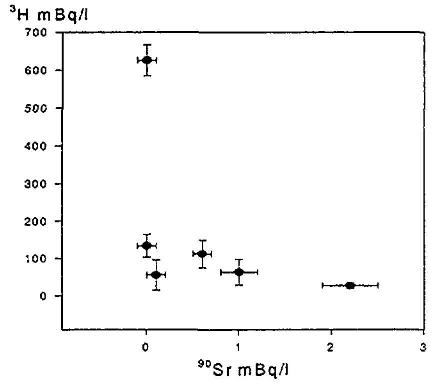

FIG. 2. The difference of activities between bottom layer and surface layer for ^{3}H compared to ^{90}Sr in Mururoa lagoon water.

While underground samples showed ^{3}H and ^{90}Sr activity concentrations in the intervals 10^{4} - 10^{10} and 1 - 10^{5} Bq/m^{3}, respectively, the surface samples collected in the lagoons showed much lower concentrations, which required very long counting times.

Fig. 2 compares the results of ^{3}H and ^{90}Sr measurements for Mururoa lagoon. The data are plotted as differences in activities between the bottom and surface layers clearly showing higher concentrations measured in bottom samples. This implies that the sources of ^{3}H and ^{90}Sr should be in the sediment. This has been well confirmed by analysing ^{3}H content of pore water extracted from the sediment. The values obtained were higher by a factor up to 3 than the ^{3}H concentration in bottom waters. While in the case of tritium, we expect that all tritium comes to the lagoon from underground sources, the case of ^{90}Sr is not so simple. It is expected that two sources may play a role : (i) a leaching of surface sediment, which still contains ^{90}Sr (as for ^{137}Cs or ^{239,240}Pu), and (ii) an underground contribution [4].

There is another interesting feature seen from Fig. 2: two stations exhibit different behaviours, one showing high ^{3}H and low ^{90}Sr concentrations and the other the contrary. The site with the lowest ^{3}H value (CRABE) has the highest ^{90}Sr concentration in water because of the high concentration of ^{90}Sr in sediment. The site with the highest concentration of ^{3}H (EXOCET) has a low ^{90}Sr concentration because of the low concentration of ^{90}Sr in sediment, suggesting an infiltration of tritium from underground sources to Mururoa lagoon.

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INDEX OF PAPER NUMBERS BY THEMATIC AREA

T01 : Mediterranean Sea

IAEA-SM-354/7, 14, 28, 49, 61, 71, 84, 87, 16P, 18P, 19P, 20P, 39P, 41P, 42P, 47P, 50P, 55P, 68P, 72P, 74P, 85P, 126P, 141P, 151P, 162P, 163P, 166P, 169P, 172P, 181P, 186P, 187P, 194P, 209P, 213P, 228P, 231P, 237P, 239P, 248P, 260P, 266P, 279P, 280P, 281P, 282P, 283P

T02 : Black Sea

IAEA-SM-354/8, 22, 23, 25, 26, 27, 28, 29, 93, 27P, 29P, 31P, 33P, 214P, 222P

T03 : Biomonitors

IAEA-SM-354/17, 18, 20, 70, 71, 16P, 18P, 20P, 21P, 25P, 45P, 48P, 68P, 72P, 101P, 123P, 124P, 125P, 147P, 148P, 155P, 158P, 169P, 178P, 193P, 213P, 221P, 224P, 228P, 230P, 237P, 240P, 242P

T04 : Quality Assurance

IAEA-SM-354/31, 32, 33, 96, 87P, 91P, 92P, 179P, 238P, 264P, 285P

T05 : Atlantic Ocean

IAEA-SM-354/44, 70, 91, 94, 101, 103, 11P, 22P, 24P, 35P, 63P, 64P, 67P, 69P, 70P, 83P, 84P, 97P, 103P, 105P, 130P, 164P, 197P, 203P, 204P, 250P, 270P, 278P

T06 : Metals

IAEA-SM-354/14, 48, 49, 50, 51, 52, 53, 71, 19P, 36P, 37P, 42P, 44P, 47P, 50P, 103P, 123P, 124P, 126P, 138P, 142P, 150P, 159P, 163P, 173P, 181P, 184P, 199P, 221P, 231P, 232P, 237P, 239P, 240P, 275P, 280P

T07 : Arctic Ocean

IAEA-SM-354/59, 91, 105, 2P, 4P, 6P, 7P, 8P, 10P, 11P, 12P, 15P, 54P, 58P, 81P, 87P, 118P, 134P, 139P, 140P, 158P, 211P, 254P, 261P, 263P, 276P

T08 : Pesticides

IAEA-SM-354/61, 63, 64, 65, 74P, 83P, 84P, 85P, 94P, 97P, 116P, 122P, 232P, 239P, 242P, 248P, 255P, 259P, 275P

T09 : Pacific Ocean

IAEA-SM-354/99, 107, 11P, 21P, 25P, 60P, 61P, 65P, 66P, 78P, 79P, 167P, 171P, 178P, 191P, 195P, 232P, 241P

T10 : Bioimpacts

IAEA-SM-354/70, 71, 73, 22P, 24P, 35P, 116P, 149P, 205P, 247P

T11 : Bombsites

IAEA-SM-354/78, 81

T12 : Hydrocarbons

IAEA-SM-354/84, 86, 87, 27P, 79P, 81P, 101P, 121P, 148P, 151P, 210P, 227P, 258P, 263P, 277P

T13 : Marine Modelling

IAEA-SM-354/98, 91, 93, 94, 96, 97, 31P, 52P, 54P, 55P, 58P, 60P, 61P, 107P, 166P, 195P, 205P

T14 : Mass Spectrometry

IAEA-SM-354/99, 101, 103, 105, 107, 109, 39P, 159P, 174P,

T15 : International Projects

IAEA-SM-354/112, 114, 116, 117, 119, 120

T16 : Antarctica

IAEA-SM-354/1P

T17 : Indian Ocean

IAEA-SM-354/75P, 150P, 199P

T18 : Geochemical Processes

IAEA-SM-354/104P, 105P, 137P, 164P, 171P, 177P, 185P, 204P, 216P, 225P, 266P

T19 : Marine Information Systems

IAEA-SM-354/109P, 143P

T20 : Radiological Doses

IAEA-SM-354/58P, 67P, 111P, 135P, 241P

T21 : In Situ Measurements

IAEA-SM-354/93P, 96P, 98P, 161P