IAEA-TECDOC-368

BEHAVIOUR OF LONG-LIVED RADIONUCLIDES ASSOCIATED WITH DEEP-SEA DISPOSAL OF RADIOACTIVE WASTES

REPORT OF A CO-ORDINATED RESEARCH PROGRAMME
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
1982–1984

A TECHNICAL DOCUMENT ISSUED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1986

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Printed by the IAEA in Austria
April 1986

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FOREWORD

The Agency sponsored this Coordinated Research Programme to improve knowledge of various long-lived radionuclides likely to be dumped in the deep sea. During 1981 the first steps were taken to organise the programme, and the precise objects were;

1. To identify and quantify the factors which control the migration and chemical forms of long-lived radionuclides in deep-ocean sediments.
2. To quantify the rate and degree of transport of the radionuclides from sediments to overlying waters.
3. To improve knowledge of the dispersion of dumped waste from the deep-sea to surface and other water bodies.
4. To determine the redistribution of radioactivity by burrowing organisms (bioturbation).
5. To develop quantitative estimates of radionuclide uptake by benthic organisms and transfer through the marine food-chain.

During the period of the programme, meetings were held in Lisbon (8-12 November 1982), Hamburg (24-28 October 1983) and Monaco (29 October -2 November 1984).

If radionuclides can diffuse from a point where they are dumped in the deep ocean to man, it is necessary to accumulate knowledge of the paths and their relative importance. This must be done for many isotopes, and the amount of research involved is therefore large. It necessarily involves prediction, since actual transfer to man from such dumpsites has not yet been demonstrated.

Because of the international character of such potential pollution, international investigation is appropriate.

The isotopes studied were mainly ^{238}Pu, $^{239,240}Pu$, ^{241}Am, ^{226}Ra, ^{210}Po, ^{90}Sr, ^{137}Cs, ^{60}Co, and ^{99}Tc.

With sediments a knowledge of the way these isotopes distribute themselves between the water and solid phase helps in predicting diffusion. This is usually considered in terms of a parameter known as "K_d". However, there has been some controversy whether that parameter is applicable when the solid/liquid ratio is very high. One study in this TECDOC considers this and the great importance of good phase separation in experimental studies. Some authors describe the actual distributions and inventories of isotopes found in sediments and in waters, while others describe work on how bioturbation has probably influenced those concentrations. Bioturbation seems to be rather more important than previously emphasized, and more work will therefore be necessary.

When radionuclides enter the water phase, at least two obvious pathways to man exist; through material ingested by fish which are then caught, or through the water carrying the radionuclides to the coast where exposure could arise through other paths. Two authors describe concentrations of various isotopes in fish, one in various trophic levels of an ecosystem which is in relatively shallow water, but contains high quantities of such radionuclides (weapon testing grounds in the Pacific) and another in a deepwater fish, which may live relatively near a dumpsite.

As regards speciation much work remains to be done, but some useful data are supplied which describe amounts of various forms of isotopes including those attached to particles in the oceans.

Investigations on areas even closer to man are described by some workers, who analysed littoral biota, such as mussels, for various radionuclides, and finally a paper gives a perspective on likely levels of ultimate transfer to man, or risk.

During the three years of this coordinated research programme the state of knowledge has advanced significantly in this area, and this document provides a review of the progress.

The authors discussed each others' contributions at the last meeting held in Monaco, but this should not be construed as meaning they have all reviewed in detail the final form of contributions as presented here.

CONTENTS

ACTINIDE SORPTION ON MARINE SEDIMENTS

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Abstract

Sorption experiments with Pu, Am and Np were carried out using deep sea sediments collected from near the North-east Atlantic dump site. Experiment times were as long as 100 days and sediment concentrations ranged from a few tens of milligrams to a few tens of grams per litre because the aim was to model diffusion within the sediments. If R_d has the same units as K_d but with no assumption of equilibrium then the Am R_d was 10^6, but that for Np only 600 for red clay and about 1000 for carbonate sediment. For Pu (R_d normally 1000) there was a decrease in R_d with sediment concentrations of greater than 10 mg l^{-1} ascribed to carbonate complexation. Calculations showed that if R_d is high, imperfect phase separation may easily produce artificially low apparent R_d values. The effect of changing the oxidation state of Pu was important. The results showed that if such isotopes in the form of waste were emplaced 20 m or more below the sediment surface, the amount ultimately reaching the surface would be negligible, at least for this clay and carbonate sediment.

1. INTRODUCTION

The disposal of high-level nuclear waste in subseafloor sediments is under investigation in several countries as an alternative to disposal on land. If cannisters containing the vitrified waste are buried in the sediments the main barrier to the final emergence of the radioactive nuclides to the marine ecosystem will be the near-surface sediments. How effective the sediments will be as a barrier will depend upon the extent to which they interact with any nuclides that escape from the waste packages. This paper is a brief summary of a series of experiments designed to study the interaction between the actinides americium neptunium and plutonium and deep-sea sediments. The work has been described in more detail in references 1-5.

The sea water/sediment system is extremely complex and in order to assess the suitability of marine sediments as a barrier to radionuclide migration it was decided to adopt an empirical approach. Thus, a set of thirteen carefully selected sediments was contacted with sea water which had been spiked with the nuclide of interest under conditions as close as possible to natural conditions and their sorption behaviour studied. The sediments were never allowed to dry out after recovery from the seabed, the temperature was maintained at 4 °C througnout the experiments and natural sea water was used. No attempt was made, however, to control the E_h and it was assumed that the effect of pressure would be small. Because the actinides may exist in several oxidation states the oxidation state distribution was determined at each stage of the experiments.

The samples were chosen to represent a wide variety of sediments occurring in the deep sea. The calcium carbonate content varied from less than 2% to 89% and X-ray diffraction was used to identify the other components present. In addition to the sediments containing calcium carbonate and various types of clays, two manganese nodules were crushed and studied in the same way as the other samples.

The reason for including these nodules in the study is that hydrous oxides of manganese and iron occur in virtually all sediments, both as discrete oxide particules and as partial coatings on other minerals and it is likely that they exert an influence on the sorptive properties of the sediments which is out of all proportion to their concentration. The ion exchange capacities of these oxides is large, but possibly more important is the fact that they themselves participants in oxidation reduction cycles and evidence is accumulating that retention of actinides in sediments is frequently the result of precipitation during redox reactions rather than by ion exchange. All the samples were characterized as fully as possible to assess whether any particular property had an effect on the sorptive properities. Thus in addition to the mineralogical analysis, chemical composition, surface areas and cation exchange capacities were determined.

The results of the sorption experiments are given in terms of the distribution ratio R_d defined as

$$Rd = \frac{\text{Concentration of a species on the solid at time of measurement}}{\text{Concentration of the species in the liquid at time of measurement}}$$

the unit used being ml/g. This is an empirical ratio and unlike the distribution coefficient, Kd, does not imply reversibility or equilibrium and no attempt is made to relate it to a specific sorption mechanism[6].

2. EXPERIMENTAL

2.1 Sample Characterization

The mineralogy of the sediments was determined by X-ray diffraction and the elemental composition by inductively coupled plasma spectroscopy after fusing with $LiBO_2$ (major elements) and by atomic absorption spectroscopy after digestion in $HF/HNO_3/HClO_4$ (minor elements). Surface areas were determined by the simplified ethylene glycol monoethyl ether (EGME) procedure[7,8] and cation exchange capacities were determined by the caesium exchange procedure described by Beetem.[9] The sodium acetate method[10] was also used on some samples and agreement between the two methods was found to be good.

2.2 Determination of Distribution Coefficients

The batch partitioning exeriments were carried out as far as possible according to the method prescribed by Relaya in the 'Task 4' Status Report.[11] K_d values reported by different laboratories for similar or even the same materials tend to differ widely and Relaya has emphasized the need for standardization.

The temperature was kept at 4°C at all times and the sea water was filtered through 0.22μ filters before use. In order to ensure that representative samples were obtained sediments were mixed with sea water to form a slurry and samples weighing between 50 and 100 mg (dry weight) were transferred by pipetting while agitating into 50 ml Oakridge-type polycarbonate centrifuge tubes. After an initial prewash in sea water they were centrifuged for 90 minutes at 7000 rpm and the supernate discarded.

Spiked sea water solutions were prepared by adding 1-2 ml of the tracer in acid solution to 500 ml sea water. The pH was readjusted to 8.2 with NaOH and the solutions left to equilibrate for several weeks. Immediately before use they were filtered through 0.22μ filters and analyzed for tracer concentration. The final concentrations in these spiked solutions were 1.8 x 10^{-9} M or 1.8 x 10^{-10} M for Am = 2 X 10^{-10} M for Pu and 3 X 10^{-8} or 1 X 10^{-12} M for Np. Even at these low concentrations the Am was not in true solution. Thus, filtration of the more concentrated solution through successive pairs of millipore filter papers showed that about 1% of the total activity was in the size range 0.1μ to 0.22μ and another 1% was in the size range 0.025μ-0.1μ. ^{241}Am, ^{235}Np, ^{237}Np and ^{238}Pu were the isotopes used in the sorption experiment. ^{235}Np concentrations were determined by counting 5g portions of liquid in a NaI well-type scintillation counter. ^{241}Am, ^{237}Np and ^{238}Pu were determined by alpha spectrometry after extraction into TTA (2-thenoyl trifluroacetone) dissolved in cyclohexane or benzene. ^{243}Am, ^{235}Np and ^{239}Pu were used as yield monitors. The oxidation state distribution was determined before and after sorption using a combination of lanthanide fluoride precipitations and solvent extraction with TTA.[2,3,5,12]

In the first set of experiments the solid/solution ratio was kept constant at 3.3g sediment/l (on a dry weight basis). Later it was found that this was a critical parameter and the results of a thorough investigation into the effect of varying solid/solution ratio are given in section 4.

3. RESULTS AND DISCUSSION

3.1 Sediment Characterization

The results of the mineralogical and chemical analyses and of the surface area and cation exchange determinations are given in Tables I and II. It can be seen that the samples fall into several categories, viz:

1. Those high in calcium carbonate and containing minor amounts of montmorillonite, quartz, and clay minerals. The calcium carbonate content of these samples ranges from 45% to 80% and, as many of the other variables show a direct relationship to this value, the samples have been arranged in order of decreasing $CaCO_3$ content.

2. Red clays. These were obtained from the mid-Atlantic at a depth of about 6000m. they are almost completely carbonate free and contain quartz and various clay minerals. Although not detected by X-ray diffraction, the chemical analysis suggests the presence of 5%-10% amorphous iron oxy-hydroxides. Although the surface area of these sediments is high the cation exchange capacity is low.

TABLE 1

Mineralogy of Sediments

Sample No	Composition		
	Major	Minor	Trace
IOS 3	Calcite		Illite, Kaolinite
M77 20	Calcite	Quartz	
10399≠7K	Calcite	Kaolinite, illite Smectite chlorite	Plagioclase feldspar
IOS 6	Calcite	Quartz Kaolinite Illite, Montmorillonite	
IOS 4	Calcite	Montmorillonite Illite Kaolinite	Quartz
IOS 5	Calcite	Quartz, Kaolinite Illite	
IOS 2	Calcite	Quartz, Illite Montmorillonite	Mixed layer chlorite
S 702	Calcite, Quartz	Illite	
SH 1578	Smectite (30 40%) Fe Oxyhydroxides (8 10%) SiO_2 as amorphous silica		
10400≠8K	Illite Quartz	Kaolinite Smectite Fe oxyhydroxides	
IOS 1	Illite Kaolinite	Quartz plagioclase feldspar Fe oxyhydroxides	Calcite (< 5%)
MV 65 1	Birnessite Todorokite	Quartz	
6269 No 2	Amorphous Mn and Fe Oxyhydroxides	δ - MnO_2	

Table 2· Chemical Composition of the Sediments.

Sample No	$CaCO_3$ %	Si %	Fe %	Mn %	Al %	Mg %	Na %	K %	Ni ppm	Cu ppm	Zn ppm	Ti ppm	P ppm	Pb ppm	CEC MEq/100g	SA m^2/g
IOS-3	89	0 7	0 6	0 05	0 85	0 18	0 55	0 31	20	68	44	150	140	10	7	24
M77-20	88	2 2	1 7	0 12	1 4	-	0 20	0 32	21	297	109	660	60	8	7	30
10399=7K	85	9 3	1 8	0 10	3 4	0 73	0 88	2 4	-	-	-	1800	250	-	17	85
IOS-6	73	1 9	1.6	0 09	2 4	0 5	0 38	0 66	35	90	65	1200	310	<5	19	54
IOS-4	69	2 7	1 8	0 07	3 0	0 57	0 55	0 96	32	90	75	1500	190	<5	17	63
IOS-5	59	3 3	2.3	0 13	3 6	0 76	0 40	1 10	49	92	87	2200	330	20	43	58
IOS 2	50	3 6	2 5	0 03	4 6	1 0	0 44	1 30	50	89	101	2300	500	20	31	131
S 702	45	5 2	3 1	0 14	5 0	-	0 44	1 13	165	63	89	2500	430	9	20	97
SH 1578	4	12 0	14 6	4 3	2 0	-	0 70	0 34	555	865	435	1100	340	75	124	396
10400=8K	3	24 6	5 0	0 32	8 8	1 68	0 63	2 5	-	-	-	5500	680	-	43	190
IOS-1	<2	7 7	5 3	0 31	6 6	1 6	0 85	2 6	109	167	137	-	690	30	45	199
MV 65 1	-	-	2 2	32 9	2 2	-	-	-	1800	1200	1340	-	-	22	100	95
6269 No 2	-	-	13 7	16 8	1 7	-	-	-	4680	1580	680	-	-	760	82	340

3. Manganese nodules. 6269 No.2 is high in amorphous iron and manganese hydroxides whereas MV 651 is composed mainly of the minerals birnessite and todorokite.

4. SH 1578, a smectite rich sediment containing amorphous silica and iron oxy-hydroxides.

3.2. Distribution Ratios

3.2.1 Americium and Neptunium.

Figures 1-4 show how the distribution ratios varied with time. For all the sediments studied they were > 10^5 for americium. Neptunium distribution coefficients were more variable, red clay giving the lowest values and the iron and manganese rich samples the highest. Apart from one red clay, all the neptunium distribution coefficients were > 10^3. Conditions used were relatively oxidizing and under more reducing conditons R_d are likely to be even higher. This means therefore that if transport is mainly by diffusion it would take Np about 10^8 years (50 Np-237 half lives) and Am about 10^{10} years (10^6 Am-241 half lives) to pass through 30m of sediment.[13-16] Americium would therefore certainly never reach the sediment/water interface and neptunium is unlikely to pose a significant hazard. Provided, therefore, that the other properties are satisfactory, all the sediments studied (with the possible exception of the red clays for neptunium) should form excellent barriers to the migration of both these nuclides.

It was found that both before and after sorption the neptunium was in the V oxidation state. Americium was presumably in the III state.

The reactions for Np appeared to be reversible (with the possible exception of the Fe-Np reaction) but desorption R_d for Am are an order of magnitude higher than adsorption R_d. This apparent difference between sorption and desorption R_d may mean that the sorption/desorption reaction is irreversible or it may be due to the presence of a poorly sorbed species in the sorption experiments.

3.2.2 Plutonium: Figure 5 shows how the distribution ratio for total plutonium changed with time and it can be seen that although sediments absorbed plutonium at different rates the final overall R_d was > 10^4 for all sediments after 12 days.

Figure 6 shows how the concentration of the various oxidation states changed with time. At the beginning of the experiment approximately 72% of the Pu in the initial spiked sea water was in the oxidised Pu(V + VI) forms. This agrees well with the values found by Nelson and Lovett for surface waters in the Irish Sea. Thus, although the Pu concentration in this spiked sea water was roughly three orders of magnitude higher than in the Irish Sea (3.1×10^{-11} M as compared with 6.7×10^{-13} M) the oxidation state distributions were similar. When sediment was added to this sea water the concentration of reduced Pu(111 + IV) dropped much more rapidly than the concentration of Pu(V + VI). Thus for sample (10400 8K) the concentration of Pu (111 + IV) dropped by more than a factor of ten during the first hour, whereas after that time the Pu(V + VI) was still more than two thirds of its original value. It is fairly meaningless to calculate distribution ratios for individual oxidation states because there may be interchange between them but it is interesting to compare R_d after one hour and to note that for Pu(III + IV) it was 3000 as compared with 50 for Pu (V + VI).

With time the oxidised Pu(V + VI) was also very efficiently removed from solution. In fact after 102 days there was more reduced than oxidised Pu in solution for all the samples. It is impossible to tell whether the Pu-V is adsorbed as Pu-V or whether it is reduced during or before sorption but it is clear that it is the rate of sorption of Pu-V which governs the rate at which the overall R_d increases with time. It is probably significant that there is a strong correlation between the rate at which Pu-V is removed from solution and the Np distribution coefficient. This is illustrated in Figure 6 where the Np R_d[15] are written next to the corresponding graphs showing the rate at which the Pu-V concentration decreases during 22 hours. This figure also illustrates the dramatic difference in the rates of sorption.

If one assumes that removal from solution is accompanied by reduction then one can rank the sediments in order of reducing ability, the order being SH 1578 > 10399 7K > 10400 8K. So, although the range in final distribution coefficients was not large, the rate at which Pu was adsorbed by the different sediments varied significantly Thus the smectite, SH 1578, adsorbed 98% of the total Pu within the first 22 hours whereas the red clay and the carbonate-rich sediment adsorbed 60% and 80%, respectively, during the same period. This rate appears to be related to the ability of the sediments to reduce plutonium from the Pu-V to the Pu-IV form.

Desorption distribution ratios were five to ten times greater than sorption distribution ratios and the proportion or reduced plutonium in solution was much the same as at the end of the sorption period. To a certain extent the high desorption distribution ratios may be explained by the presence of some non-sorbable spieces (e.g. organic complexes or micro-plarticulates that were not removed during phase separation) which lowers the observed sorption Rd more than the desorption Rd. However, differences of this magnitude probably indicate that the sorption-desorption reaction is, at least to some extent, irreversible.

Edgington,[17,18] by comparing the K_d values reported in the literature has ranked the actinides in order of decreasing distribution coefficient as follows:

$$Th(IV) = Pu(IV) = Am(III) > U(VI) >> Np(V)$$

This ranking was based on the results from a number of different sediments studied under different conditions. As a result of the present work we now have a complete set of R_d values for Pu, Am and Np all determined under identical conditions and on the same sediments and these values for both sorption and desorption are given in Table 3. Included in Table 3, on the assumption that

Table 3 Relationship between distribution ratios and the rate at which Pu V is removed from solution by the different sediments.

Sample	"Reducing Power as indicated by percent Pu V remaining in Solution after			Distribution Ratio ml/g				
				Np	Pu		Am	
	1hr	2hr	30d	sorption and desorption	sorption 102 d	desorption	sorption 56 d	desorption
SH 1578	31	1	0 1	7×10^3	9×10^4	4×10^5	4×10^5	26×10^5
0399 7K	59	27	0 7	3×10^3	6×10^4	2×10^5	2×10^5	$- 6 \times 10^5$
10400 8K	89	47	3 7	$0\ 3 \times 10^3$	5×10^4	2×10^5	1×10^5	$- 6 \times 10^5$

this is a measure of the ability of the sediments to reduce the actinides, is the percent of Pu-V remaining in solution after the different time intervals. Of course, this may not be a valid assumption and thse figures may simply be an indication of the relative ability of the different sediments to adsorb pentavalent actinides.

4. The Effect of Solid/Solution Ratio on the Measured Distribution Coefficient

In all the work described so far a solid/solution ratio of 3.3 g/l was used. However, in the disposal situation this ratio will, of course, be much higher and it was decided to investigate the effect of increasing this ratio. The results showed two important effects. One, specific to plutonium on high-carbonate sediments has important implications from the waste management point of view and the other which applies to all high Rd species highlights some of the problems associated with the determination of distribution coefficients by the batch method.

4.1 Plutonium on high-carbonate sediments.

Two sets of samples of the high-carbonate sediment, 1039 7K were shaken with sea water which had an initial concentration of 35000 Bq/1 (2.33×10^{-10} M) ^{238}Pu. The solid/solution ratio ranged from about 0.002 to 0.2 (2g/1 - 200/1) and a series of experiments were carried out on them. Phase separation was always carried out by centrifuging for 90 mins at 7000 rpm. (5280g) followed by filtration through 0.22μ milipore filters.

The first set of sediments was i) analysed after 24 days and the distribution ratios calculated. ii) the supernate remaining after the first sorption was transferred to tubes containing 0.1g quantities of fresh sediment and a second distribution ratio determined. iii) Fresh unspiked sea water was added to the loaded sediment and the desorption distribution ratio was measured.

The second set of sediments was (i) analysed after 29 days (exactly 5g of the solution phase removed) for reduced Pu(III + IV) and oxidised Pu(V + VI) as well as total Pu, (ii) after 128 days the solution phase was again analysed but this time the excess solution was added to fresh sediment keeping the solid/solution ratio the same as in the original sorption experiments.

Table 4 shows the three sets of distribution ratios together with the percent reduced Pu in solution after phase separation. It can be seen that for solid/solution ratios greater than about 0.04 (40g/1) the distribution ratios were remarkably low (100 to 200 ml/g instead of the usual $>10^4$ ml/g) and there was no significant increase in R_d as the contact time increased from 24 to 128 days. Furthermore, at these high solid/solution ratios the plutonium in solution was virtually all in the oxidised (V + VI) forms. At low solid/solution ratios, on the other hand, the plutonium was mostly in the reduced (III + IV) forms and distribution ratios were greater than 10^4. For the two samples containing the least sediment the distribution ratio after 129 days did seem to be significantly greater than after 29 days.

We thus have the situation that in carbonate sediments plutonium behaves quite differently at high and low solid/solution ratios. The obvious explanation is that at high solid/solution ratios carbonate complexes are formed which are sorbed less strongly than are PuO_2^+ and $Pu(OH)_3^+$ which are the forms in which plutonium exists in sea water in the absence of sediment.[18, 19, 20] No attempt was made to determine whether the

Table 4 Pu Oxidation State Distribution During Sorption

Sample	Time	Pu-238			Concentration (Bq/l) during sorption				Ratio
		Total	(III + IV)	V + VI	(III+IV+V)	IV	III	VI	V + VI / III + IV
Initial Sea-water 3 1 x 10^{-11}M		4356 ± 1421	1242 ± 120	3366 ± 144	4656 ± 186	1200 ± 138	42 ± 183	-	2 7 ± 0 3
SH 1578	1 h	1026 ± 171	103 ± 3	1053 ± 316	1022 ± 129	90 ± 10	13 ± 11	-	10 2 ± 3 1
	22 h	88 ± 8	36 ± 2	44 ± 3	89 ± 2	46 ± 2	-10 ± 3	-	1 2 ± 0 1
	30 d	24 ± 2	19 ± 2	2 4 ± 0 7	21 ± 1	20 ± 1	- 1 ± 2	1 5 ± 0 6	0 1 ± 0 04
	102 d	24 ± 2	17 ± 1	4 8 ± 1 4	24 ± 2	19 ± 1	- 2 ± 2	0 3 ± 0 3	0 3 ± 0 1
10399 7K	1 h	2416 ± 98	107 ± 11	1983 ± 88	2364 ± 709	80 ± 5	28 ± 12	-	19 ± 2
	22 h	855 ± 41	49 ± 2	897 ± 51	766 ± 42	43 ± 2	5 ± 3	-	18 ± 1
	30 d	34 ± 3	19 ± 2	22 ± 2	44 ± 25	18 ± 1	1 ± 2	1 4 ± 0 5	1 ±0 2
	102 d	20 ± 1	13 ± 1	6 ± 2	20 ± 2	14 ± 2	-1 ± 2	0 9 ± 0 3	0 5 ±0 2
10400 8K	1 h	2982 ± 895	128 ± 6	3011 ± 109	2909 ± 146	64 ± 14	64 ± 15	-	24 ± 1
	22 h	1724 ± 35	68 ± 4	1589 ± 180	1345 ± 61	65 ± 6	4 ± 7	-	23 ± 3
	30 d	122 ± 15	17 ± 1	126 ± 6	98 ± 9	21 ± 2	-4 ± 2	12 ± 2	7 ± 1
	102 d	26 ± 2	14 ± 1	8 ± 1	24 ± 1	17 ± 1	-3 ± 2	1 ± 1	0 6 0 1

plutonium was in the V or the VI form but the fact that neptunium did not behave in the same way indicates that we were probably dealing with Pu(VI) complexes, since neptunium has been shown to be in the V form in sea water and in our laboratory experiments. This is in agreement with the predictions of Skytte Jensen[21] which give $PU_2(CO_3)^{2-}_2$ and $PUO_2(CO_3)$ as the most likely carbonate species at PH 8 and Eh about 400 mv. The bicarbonate $Pu(O_2)(OH)_2(HCO_3)^{1}$ may also be present. Sullivan and Woods22 have studied the interaction of Pu(IV) with bicarbonate and concluded that in sea water soluble Pu(VI) would exist in roughly equal amounts as $PuO_2(OH)_2$ and $Pu(OH)_2(HCO_3)^{-1}$ with about 15% as Pu O_2 $(CO_3)2-_2$.

When the solution phase remaining after the first Rd determination was contacted with fresh sediment the results depended on whether the solid/solution ratio was kept high or whether it was lowered for the second Rd determination. If the solid/solution ratio was high for both the first and second sorptions the distribution ratio was the same both times and virtually all the plutonium was in the oxidised (V + VI) forms after both sorptions. This must mean either that only one plutonium species was present in solution or that equilibrium between different species was rapidly re-established as one species was removed from solution.

If the solid/solution ratio in the second sorption was low the distribution ratio rose to $>10^3$ and the percentage of oxidised Pu(V + VI) dropped. Clearly, therefore, in the absence of large quantities of sediment some of the plutonium carbonates have reverted to more readily sorbable species.

4.2 Effect of the presence of some "low-Rd" species.

It was found experimentally that in many cases the observed Rd decreased as the solid/solution ratio was increased. This effect has been observed by other workers and various explanations offered. We considered that the most likely explanation was that some "low-Rd" species was present. It would remain with the solution phase and lower the observed overall Rd. This low-Rd species could be in the form of complexes with organic matter or anions such as carbonates or it could simply be micro-particulates which remained with the liquid phase during phase separation. These micro-particulates could be true colloids but are more likely to be fine particles of sediment or iron and manganese oxy-hydroxides to which the nuclides have sorbed.

In order to assess the effect that the presence of such low-Rd species would have on the measured Rd a series of theoretical calculations were carried out and graphs showing the effect that small amounts of a low-Rd species will have on the observed Rd are given in Figures 7 and 8. It is frequently convenient to plot log (Co - C)/C rather than log Rd against Log m/v (where Co and C are the initial and final concentration in solution, respectively, and both sets of graphs are given.
It can be seen from Fig 7 that if the Rd of the high-Rd species is as high as 10^6 then very small amounts of a low-Rd species have a marked effect on the measured Rd. Figure 8 shows that the effect of a small amount of low-Rd species decreases with decreasing Rd. Thus 0.05% of a species with Rd=0.1 will have no detectable effect if the Rd of the high-Rd species is 10^3 or less.

Figures 11-13 show the effect of varying the solid/solution ratio on the experimentally determined Rd for Am, Np and Pu on different sediments. Superimposed on the experimental curves are theoretical graphs that best fit the observed graphs. For Am and Pu it is possible to fit the experimental graphs very closely to theoretical ones assuming the presence of between 0.1% and 0.3% of a low-Rd species. Similar amounts of low-Rd Np species may also be present but the lower Np Rd means that these samll amounts would not be detected.

The experiments in which "second Rd" were determined confirmed our conclusion that the presence of some low-Rd species was causing the drop in measured Rd for Am and Pu (apart from Pu on high-carbonate sediments). Distribution ratios obtained when the solution removed after the first Rd determination was contacted with fresh sediment were several orders of magnitude lower than values obtained for the same solid/solution ratio when the fresh spiked sea water was used. Second Rd for Np were the same as the first Rd, presumably because the amount of low-Rd species was too low for detection.

Summary and Conclusions

From the waste disposal point of view we are now in a position to assess much more accurately the likely mobilities of the three nuclides studied and to make reccommendations as regards future research. Modellers must bear in mind the possibility that R_d obtained using the batch method might have been affected by the presence of micro-particulate or complexed material. In general the effect of such materials will be to lower the observed R_d of the main species and hence predictions based on such results will be conservative. However, the mobilities of the micro-particulates and complexes themselves (assuming that some of them, at least, are not simply generated during shaking) must also be considered. They are likely to be neutral or negatively charged and could travel a considerable distance before being converted to a more readily sorbed form.[23, 24]

Looking at each element individually we can conclude that -
(1) Americium is the least likely of the three elements studied to escape from the sediments. On both sediments more than 99.95% was sorbed with a R_d of 10^6 and the small amount of nuclide that did not appear to be sorbed was almost certainly colloidal. There is evidence[25, 26] that carbonate complexes of americium are present in natural waters. However, these are likely to be in equilibrium with the main positively charged trivalent species and will therefore be sorbed soon after the bulk of the americium is removed from solution. Sandia[22] have developed computer codes for use in sensitivity studies of radionuclide migration in deep-sea sediments and, using risk methodologies developed for the US Environmental protection Agency, have calculated the minimum permissable Kd as a function of burial depth for a number of radionuclides. These "critical Kd" are listed in Table 5 and it can be seen that the critical Kd for americium, even at a burial depth of 2m, is two to three orders of magnitude lower than our measured R_d.

It is recommended, therefore, that investigations into the behaviour of americium be given a low priority in future research except where its tendancy to remain in the III oxidation state makes comparisons with the other actinides of interest. The readiness with which it forms colloids could also be exploited in colloidal studies.

<u>Table 5</u> Critical K_d for isotopes of Am, Np and Pu in ml/g (from Sandia, 1983 Status Report27).

	Burial Depth (m)				
	2	5	10	20	30
Am - 241	10^3	10^3	10^2	10	10
Am - 243	10^4	10^3	10^2	10^2	10
Pu - 238	10^2	10	0	0	0
Pu - 239	10^3	10^2	10^2	10	1
Pu - 240	10^3	10^2	10^2	10	10
Pu - 242	0	0	0	0	0
Np - 237	10^3	10^3	10^2	10	10

(2) Plutonium : Because of its complex chemistry plutonium is always likely to provide surprises and investigations into its behaviour should continue. The fact that the R_d for high-carbonate sediments dropped so dramatically with increasing solid/solution ratio emphasises the fact that site-specific studies are necessary, that experimental results cannot be extrapolated from one sediment type to another and that it is not possible to predict the behaviour of one actinide from that of the

others (or from chemical analogues such as the rare earths). Although at first sight this low R_d is disconcerting, it is not necessarily diasasterous. The main plutonium isotopes have reasonably short half lives and it can be seen from Table 5 that the critical K_d for a burial depth of 20m is only 10 ml/g which means that an R_d of 100 ml/g gives a satisfactory safety margin provided that the waste is placed 20m or more below the sediment surface.

From the waste management point of view it is clear that Pu oxidation state is not important. Plutonium, whether originally present in reduced or oxidised form was strongly sorbed by all three types of sediment studied, final overall distribution coefficients being $> 10^4$ in all cases.

(3) Neptunium: Neptunium R_d did not decrease with increasing solid/solution ratio probably because Np has a relatively low R_d and small amounts of a low-R_d species would not have been detected. Because 237Np has such a long half-life and because it is poorly sorbed to many geological materials it is generally considered to be the actinide most likely to find its way back into the environment. However, we have consistently found that the R_d for carbonate sediment is $>10^3$ ml/g wich means that even a 2m burial depth would be satisfactory in this sediment type (Table 5). The R_d for the red clay was only 600 and even lower values have been reported by others e.g. Fowler et.al.[28] A burial depth of at least 20m would be necessary in this type of sediment. Under the relatively oxidising conditions used in these experiments the Np in solution was in the V state. Under more reducing conditions it may be reduced to Np-IV and the distribution ratio would almost certainly rise.

Table 6 Effect of Solid/Solution Ratio - Summary of Results.

	RED CLAY - 10040#8K			CARBONATE SEDIMENT 10399#7K		
	Sorption	Desorption R_d	Second Sorption R_d	Sorption	Desorption R_d	Second Sorption R_d
Am	R_d increased with decreasing solid/soln ratio. Levelled off at 10^6 ml/g. % non-separable ~0.03, (0.22 μ filters) ~ 0.02% (0.10 μ filters).	> Sorption R_d	<< 1st R_d	R_d increased with decreasing solid/soln. ratio Levelled off at 1×10^6 - 2×10^6 % non-separable ~0.05% (0.22 μ filters). 0.02 - 0.03% (0.10 μ filters).	> Sorption R_d	<< 1st R_d
Np	R_d constant at about 480 ml/g for solid/soln. ratio > 0.016. Increase for two lowest solid/soln. ratios (580 → 750 ml/g) % non-separable < 0.2% (0.10μ filters).	> Sorption R_d Difference greater for lower solid/soln. ratios.	Same as first R_d for high solid/soln. ratios.	R_d constant for all solid/soln. ratios. % non-separable <0.5% (0.10 μ filters).	≈ Sorption R_d	≈ 1st R_d
Pu	R_d increased with decreasing solid/soln. ratios. Levelled off at 7.9×10^4 ml/g. % non-separable ~ 0.05% (0.22μ filters)	> Sorption R_d	<< 1st R_d Difference greatest at high solid/soln. ratios.	High Solid/Solution Ratios.		
				R_d low i.e. 100-300 ml/g All in Pu(V+VI) form.	≈ Sorption R_d All in Pu(V+VI) form	≈ 1st R_d
				Low Solid/Solution Ratios.		
				$R_d > 10^4$ ml/q. Mostly in Pu(III + IV) form.	> Sorption R_d Mostly in Pu(III + IV) form.	<< 1st R_d

ACKNOWLEDGMENT

The work described in this report has been carried out for the Department of the Environment as part of its radioactive waste management research program. The results will be used in the formulation of Government policy but at this stage do not necessarily represent that policy.

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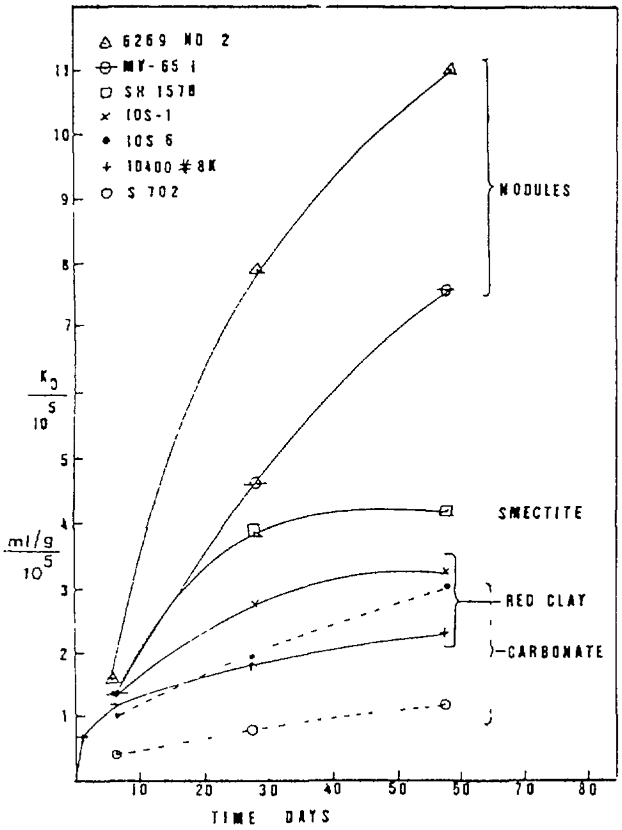

FIGURE 1 Americium Distribution Coefficients

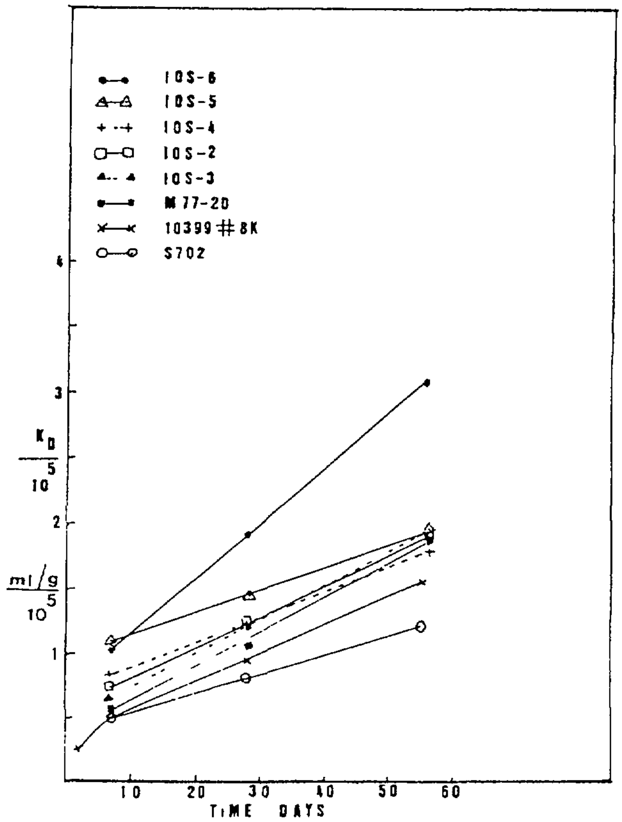

FIGURE 2. Americium Distribution Coefficients High-Carbonate Sediments

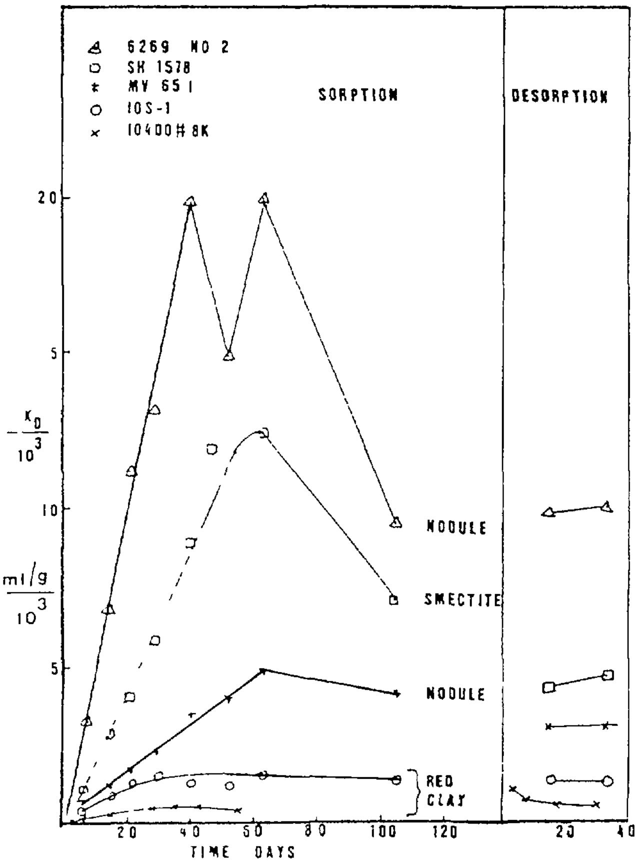

FIGURE 3 Np Distribution Coefficients Low-Carbonate Sediments

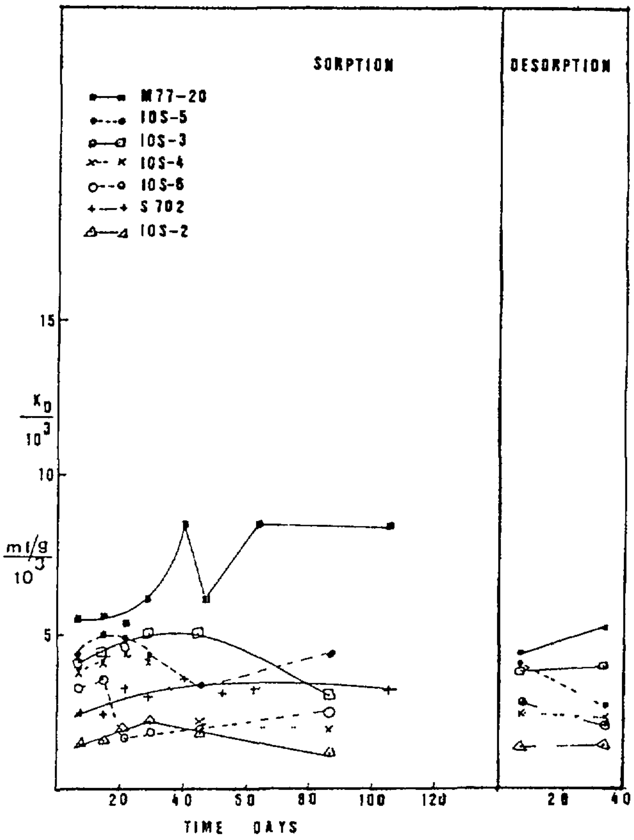

FIGURE 4 N_p Distribution Coefficients High-Carbonate Sediments

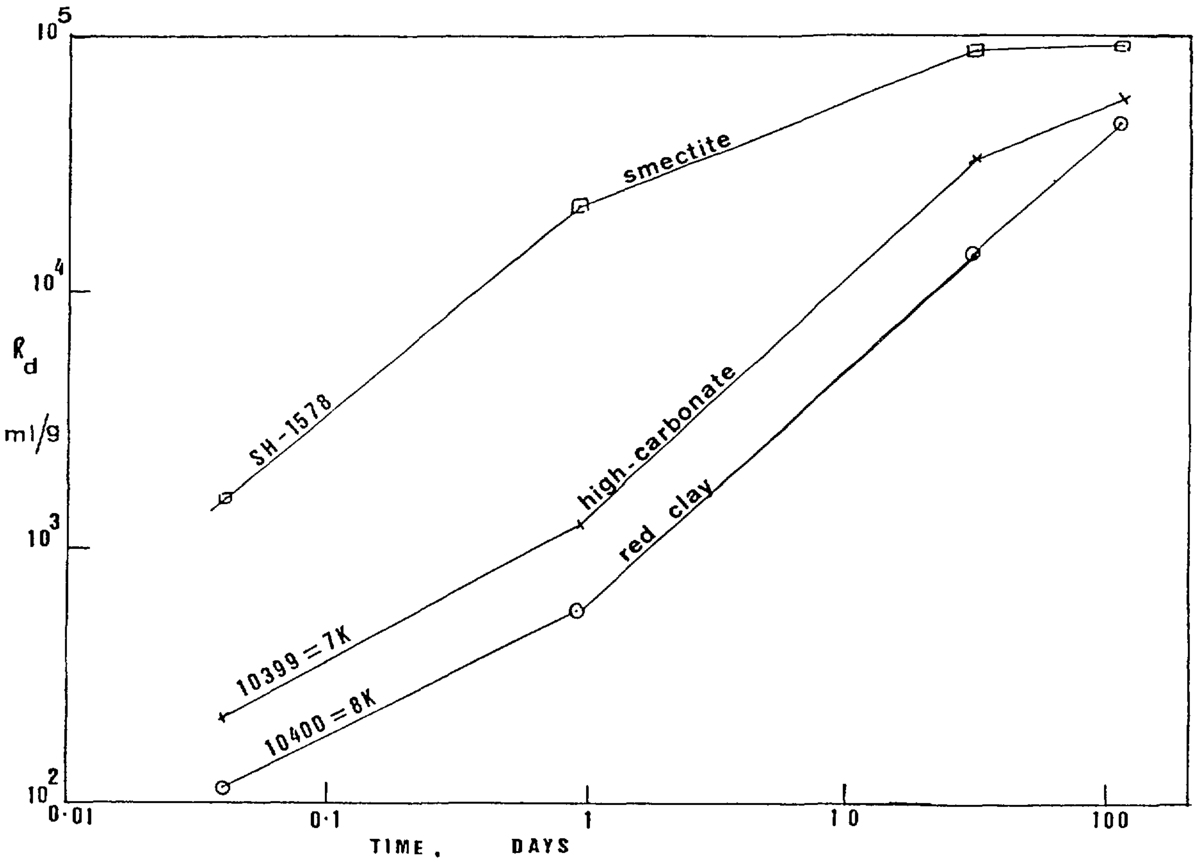

FIGURE 5. PLUTONIUM DISTRIBUTION COEFFICIENTS

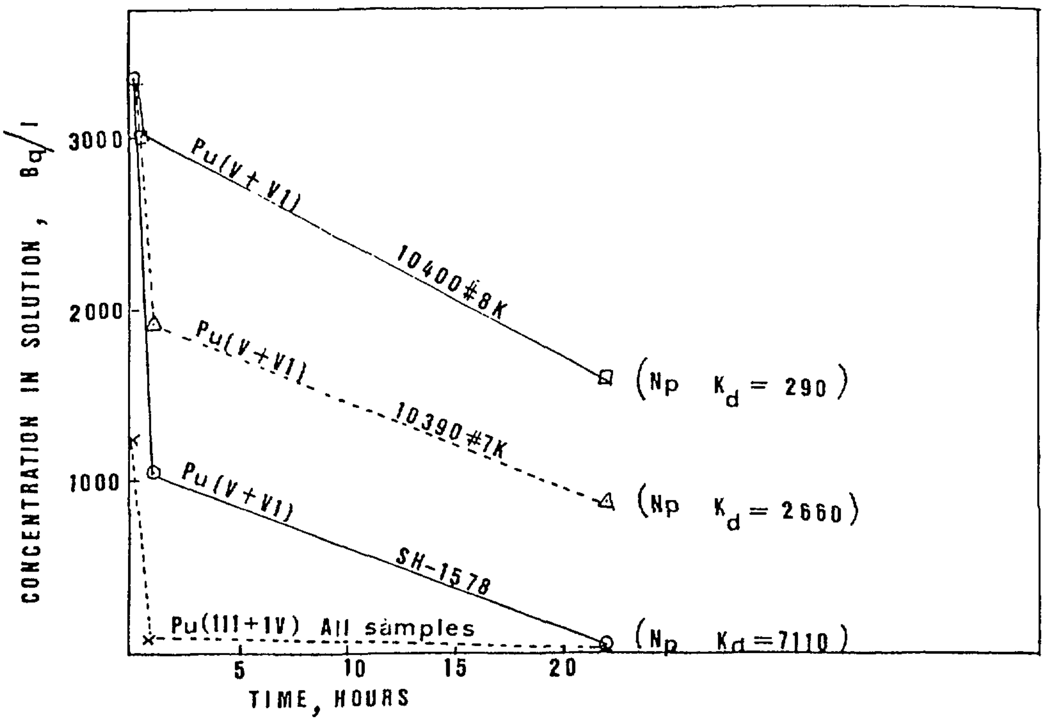

FIGURE 6. CONCENTRATION OF OXIDISED & REDUCED PLUTONIUM-238 IN SOLUTION DURING THE FIRST 22 HOURS

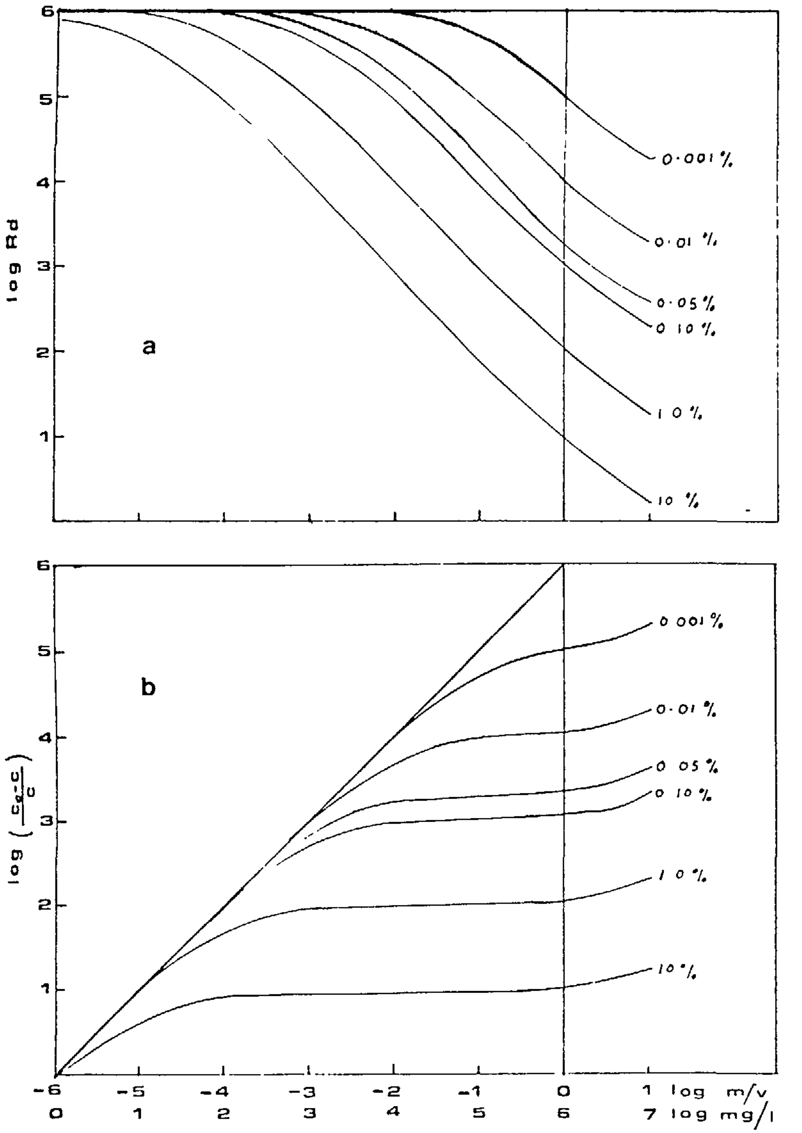

Fig. 7 The effect of a fixed proportion of a second species which is not adsorbed by the sediment on the relationship between log m/v and (a) log R_d (b) log(C_o - C)/C for different percentages of low R_d species ($R_H = 10^6$, $R_L = 0.1$).

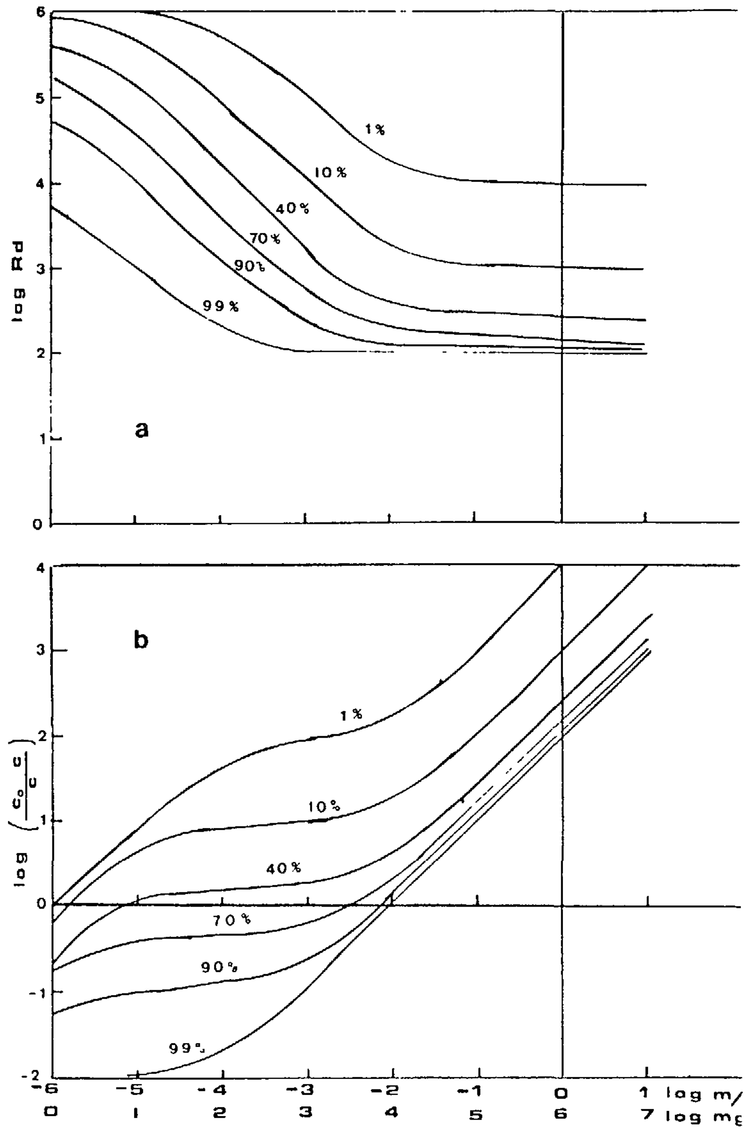

Fig 8 The effect of a fixed proportion of a second species with Rd=100 on relationship between log m/v and (a) log Rd (b) Log(Co-c)/c for different percentages of low Rd species. ($R_H = 10^6$, $R_L = 10^2$).

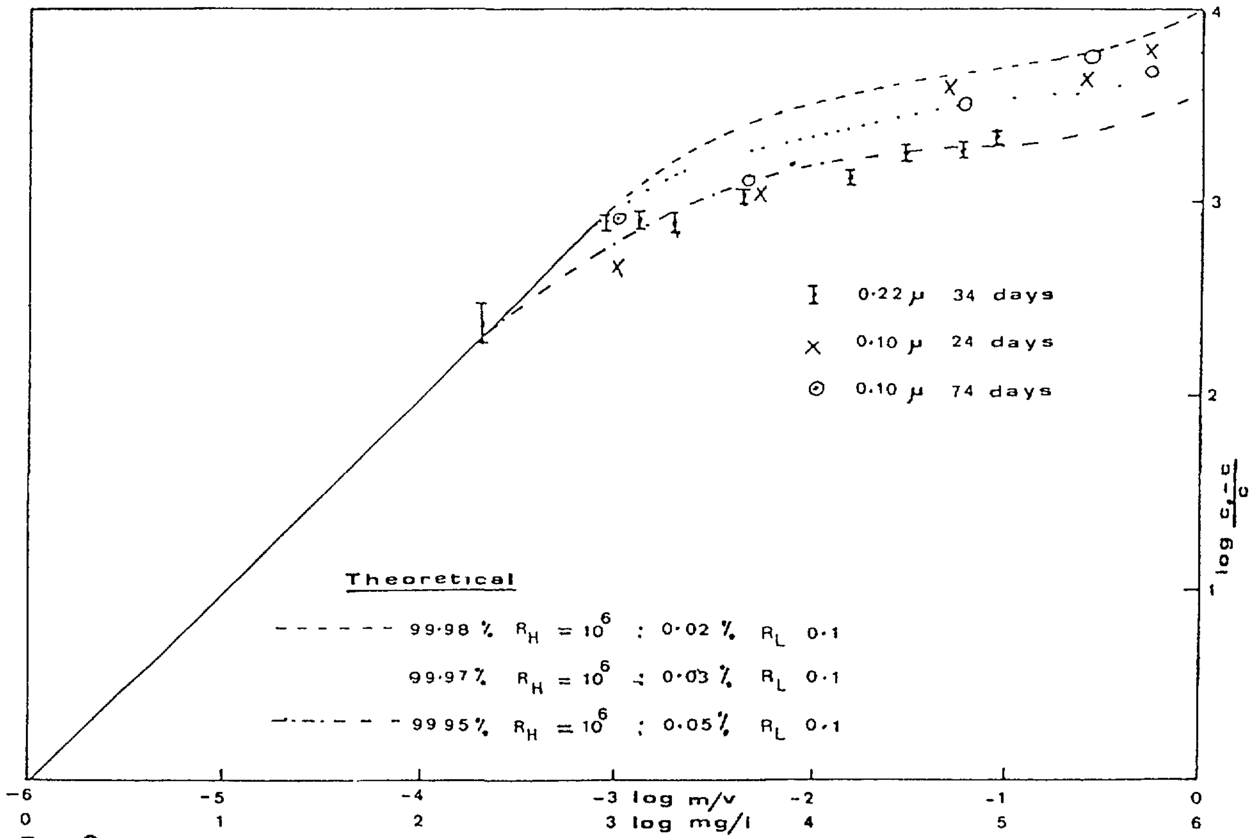

Fig. 9 Effect of solid/soln ratio on the value of log (Co-c)/c for americium on the high-carbonate sediment 10399#7K

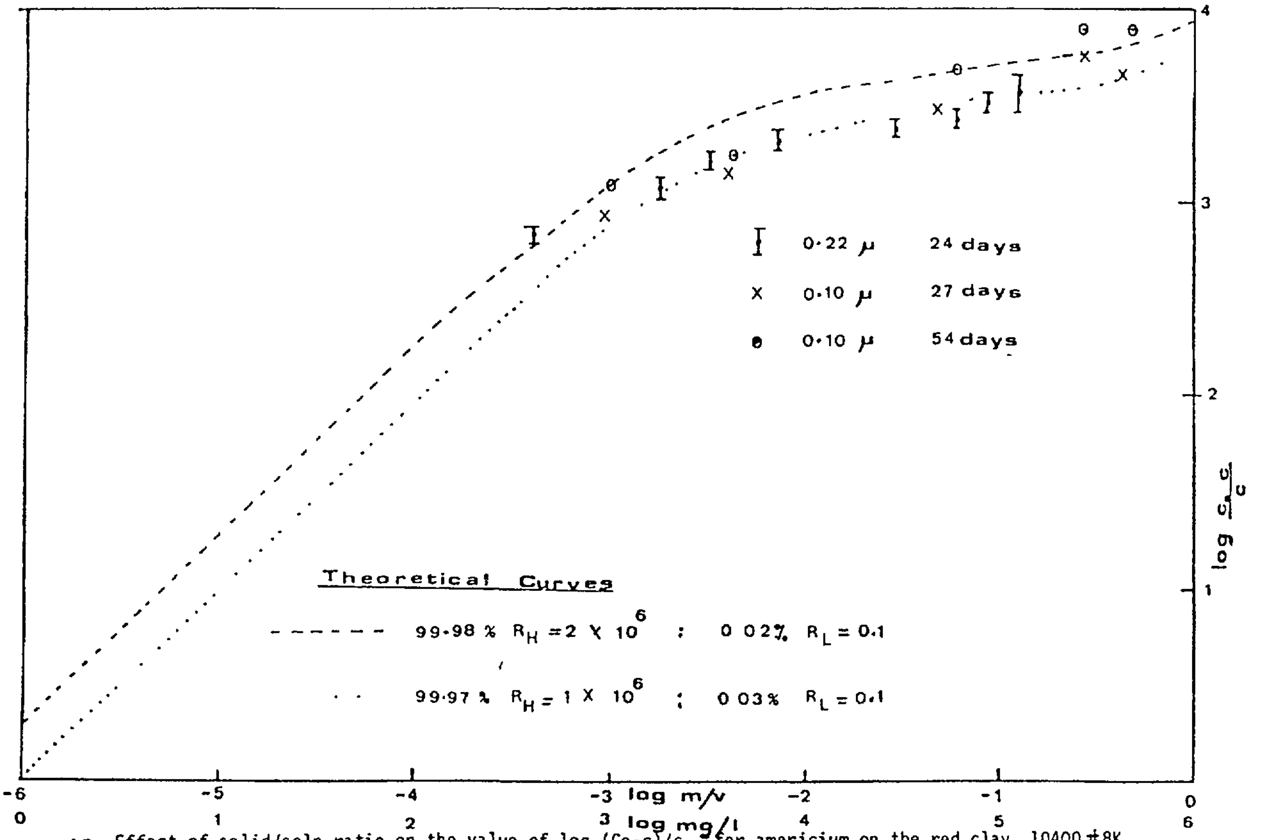

Fig. 10 Effect of solid/soln ratio on the value of log (Co-c)/c for americium on the red clay, 10400#8K.

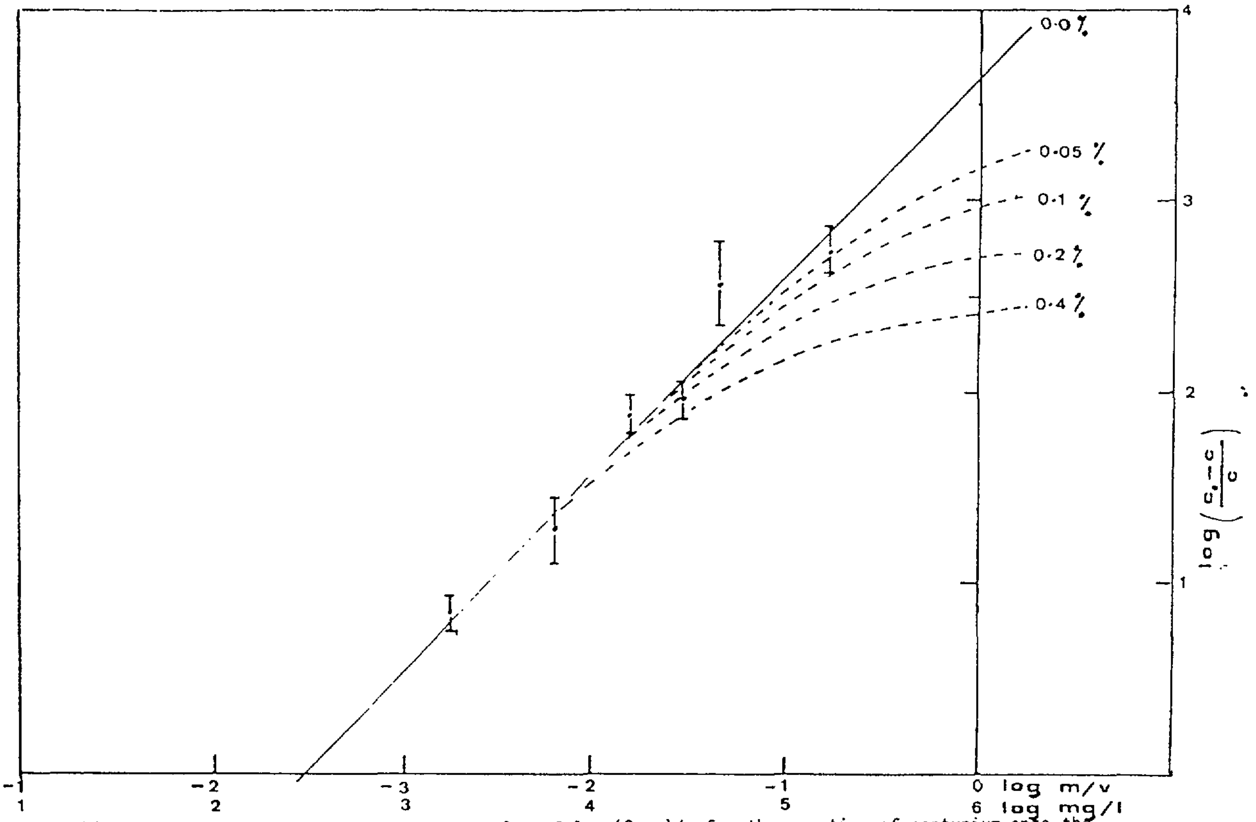

Fig. 11 Effect of solid/soln. ratio on the value of log (Co-c)/c for the sorption of neptunium onto the hig-carbonate sediment 10399 # 7K. Dotted lines represent theoretical curves for different percentages of a non-separable species. (R_H = 3980, R_L = 0.1)

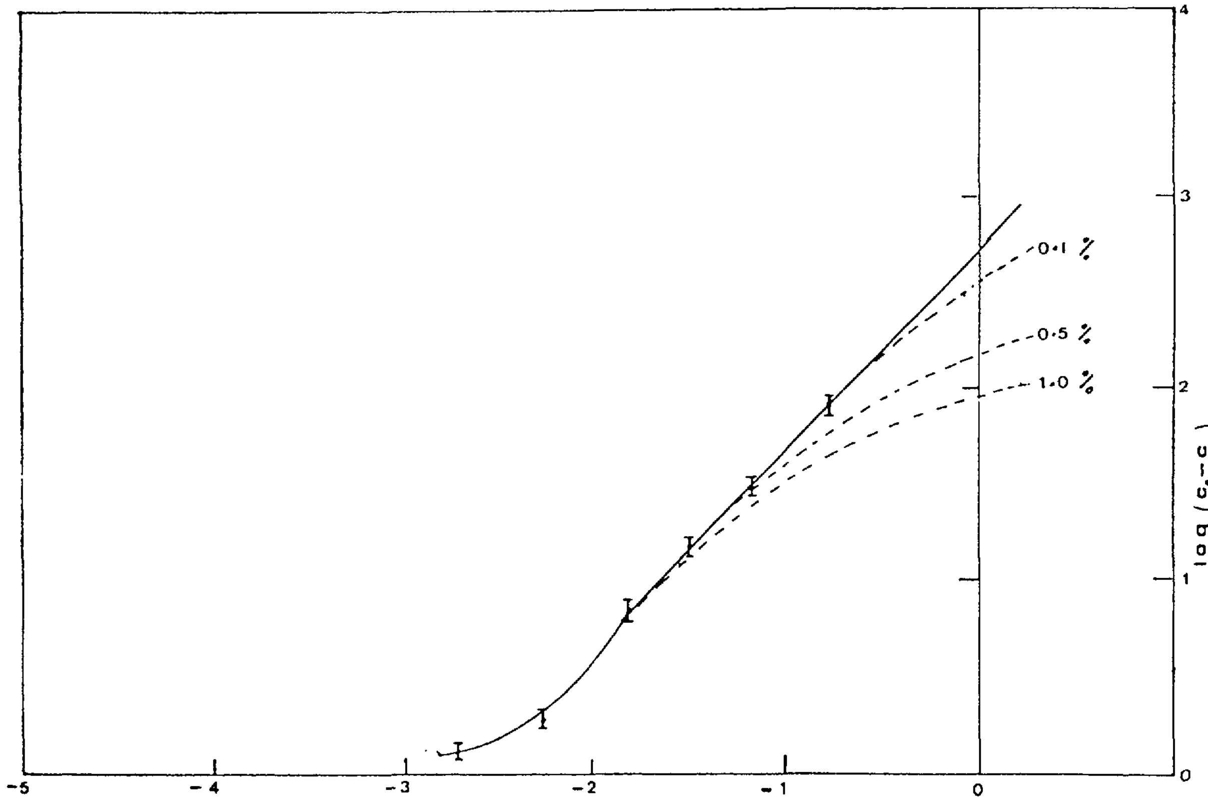

Fig. 12 Effect of solid/soln ratio on the value of log (Co-c)/c for sorption of neptunium on red clay, 10400 # 8K. Dotted lines represent theoretical curves for different percentages of a non-separable species (R_H = 500, R_L = 0.1).

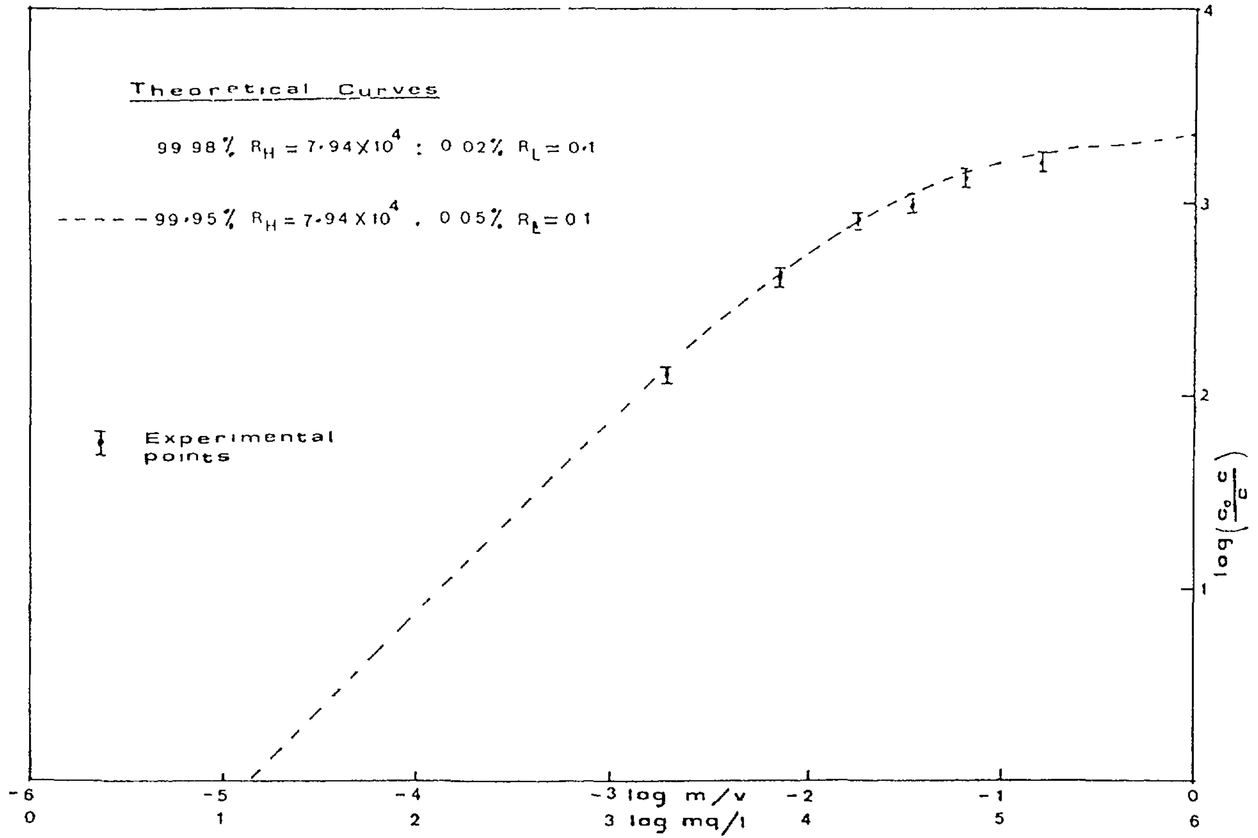

Fig. 13 Effect of solid/soln ratio on the value of log(Co-c)/c for the sorption of plutonium on red clay, 10400 # 8K

FALLOUT PLUTONIUM IN WESTERN NORTH PACIFIC SEDIMENTS*

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Abstract

The study compared sediment samples from the Mid-Pacific Gyre area north of Hawaii and from the Western North Pacific. The latter had from 2 7-5.5 the concentrations of Pu isotopes compared with the former, but the profiles with depth were similar. The increased levels were probably due to close-in fall-out from the Marshall Islands weapons tests. The inventories for water column plus sediment were 4 0-4.3 mCi km^{-2} for NW Pacific and 2.9 for the Mid Pacific area. The proportions in the sediments are respectively 8% and 2%. Evidence is presented that close-in fallout was more available to scavenging For NW Pacific, significant bioturbation effects were seen, redistributing Pu as deep as 46 cm, even though these sediments are abyssal. This implies subsurface waste disposal may be more vulnerable to the effects of bioturbation than previously supposed

1. Introduction

The results[1] of transuranic analyses of water samples collected as part of the GEOSECS program in the North Pacific revealed two features found at stations throughout much of this ocean area.

A. A subsurface maximum in Pu concentration centered at about 500 m.

B. A near bottom maximum in Pu concentration--especially in Western, Central and Northern locations. No sediment samples were collected in the GEOSECS program so there were no observations about the delivery of transuranics to Pacific sediments.

This report describes subsequent studies of the contrast between the sediment distributions of transuranics in Western N. Pacific sediments compared to that found at the MPG-1 (Mid-Pacific Gyre) study site north of Hawaii. The latter site has received study in connection with the U.S. Subseabed Disposal Program which has been assessing the technical feasibility of the use of deep ocean sediments for the disposal of high level radioactive wastes. Some of the results of fallout nuclide analyses of sediment cores from the MPG-1 site were discussed in an early CRP technical report.[2] This report also included some discussion of the fallout profiles in the sediments in the context of bioturbational mixing in the sediments at the site.

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* IAEA CRP Research Agreement No 3246/RI/CF

2. Sample Collection and Analysis

In May 1980, a series of large diameter (21 cm) gravity cores were collected on a cruise of R/V HAKUHO MARU from Tokyo-Honolulu. The corer was mounted on a tripod assembly permitting slow penetration of the sediments with the corer maintained in a vertical position.[3] The locations at which core samples were collected are indicated in Figure 1--as cores numbered 1-4. Also shown in this figure is the general location of the MPG-1 site, where earlier studies were carried out, and one coring station occupied by R/V KNORR in July 1978.

The methods used for extruding and sectioning the cores and performing the radiochemical analyses for ^{239,240}Pu have all been summarized or referenced in a recent publication.[4] Some discussion of data quality assurance also appears, or is referenced, in this publication, both in terms of general philosophy and specific examples. This laboratory has continued to participate in both national and international intercalibration exercises of radiochemical quality assurance, including recent exercises organized by the IAEA Monaco laboratory. Our performance in these exercises continues to give us confidence that our data are of high quality.

3. Results

The results of the radiochemical analyses of these Western N. Pacific sediment cores are tabulated in Tables 1 and 2--together with the positions and depths of sampling. ^{238}Pu was also measured when detectable, together with several other fallout nuclides. The ratios ^{238}Pu to ^{239,240}Pu in the cores fell in the range 0.02-0.06. In core #3, there appeared to be a trend

TABLE 1 PU IN WESTERN PACIFIC SEDIMENTS
(R/V HAKUHO MARU - MAY 1980)

Core No. :	1		2	
Latitude :	39°58'N		39°01'N	
Longitude :	156°01'E		166°02'E	
Water Depth:	5530 m		5600 m	
	Sediment Section (cm)	^{239,240}Pu*	Sediment Section (cm)	^{239,240}Pu*
	0-1	857±38	0-1	863±28
	2-3	162±15	1-2	657±23
	4-5	80±8	2-3	343±15
	8-9	6.7±3.3	4-5	262±15
	13-15	0.7±0.7	6-7	75±7
	19-21	0.8±0.7	9-10	73±10
	Bottom=29 cm		13-15	128±9
			17-19	21±2
			21-23	21±3
			31-33	1±1
			Bottom=60 cm	

---

* ^{239,240}Pu mBq/Kg (dry weight).

TABLE 2 PU IN WESTERN PACIFIC SEDIMENTS
(R/V HAKUHO MARU - MAY 1980)

Core No. :	3	4
Latitude :	38°00'N	30°00'N
Longitude :	179°45'W	170°00'W
Water Depth:	5520 m	5432 m

Sediment Section (cm)	^{239,240}Pu*	Sediment Section (cm)	^{239,240}Pu*
0-1	1378±43	0-2	164±8
1-2	802±25	2-3	75±6
2-3	430±32	3-4	91±7
3-4	380±13	5-6	115±10
4-5	218±20	7-8	90±7
5-6	180±7	9-10	58±22
7-8	87±11	13-15	40±4
9-10	41±8	19-21	5±2
10-12	34±3	31±33	1±0.5
14-16	11±2	Bottom=68 cm	
18-20	10±3		
24-26	12±2		
30-32	0.7±0.5		
36-38	0±1		
42-44	6.3±2.7		
44-46	4.3±1.0		
46-48	-0.7±1.8		
Bottom=60 cm			

* ^{239,240}Pu mBq/Kg (dry weight).

of decreasing ratios from the sediment/water interface--the upper two centimeter sections lying in the range 0.04-0.06, whereas the sections from 3 to 6 centimeters lay in the range 0.02-0.03.

The total inventory of ^{239,240}Pu found in each core was calculated by summing the amounts found in each section on a unit area basis. The results of these calculations are plotted in Figure 1 for each core besides its location.

4. Discussion

4.1 Concentrations and Inventories in Northwest and Northeast Pacific Sediments

Figures 1-2 contrast the differences in Pu concentrations and inventories at the Western Pacific stations with those from the MPG-1 area. It is clear that the inventories and, especially, the concentrations of Pu are much higher in the sediments from the Western Pacific stations. The inventories range from 2.7-5.5 times the mean MPG-1 value (excepting core 4 which is closer in all respects to those from MPG-1), while the concentrations of Pu in the 0-1 cm sediment section range 6-10 times higher. The depth distribution pattern of the nuclides in these Western Pacific sediments is not markedly different from those found in the MPG-1 region.

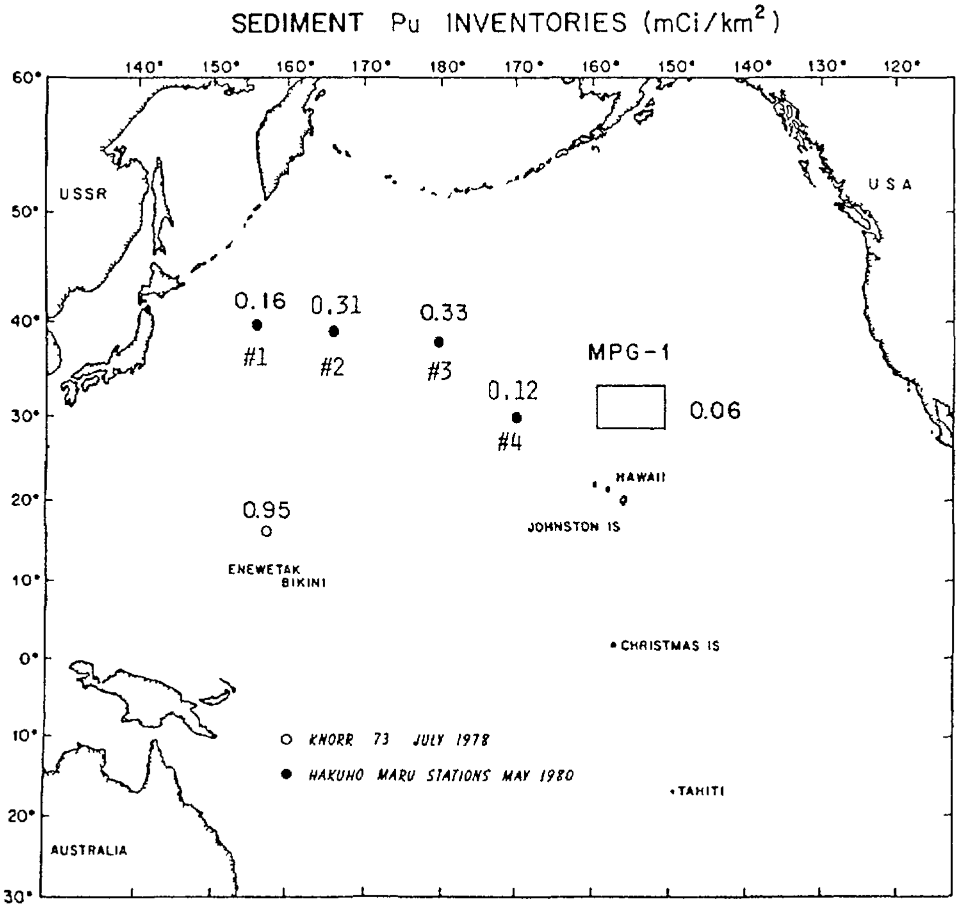

FIGURE 1

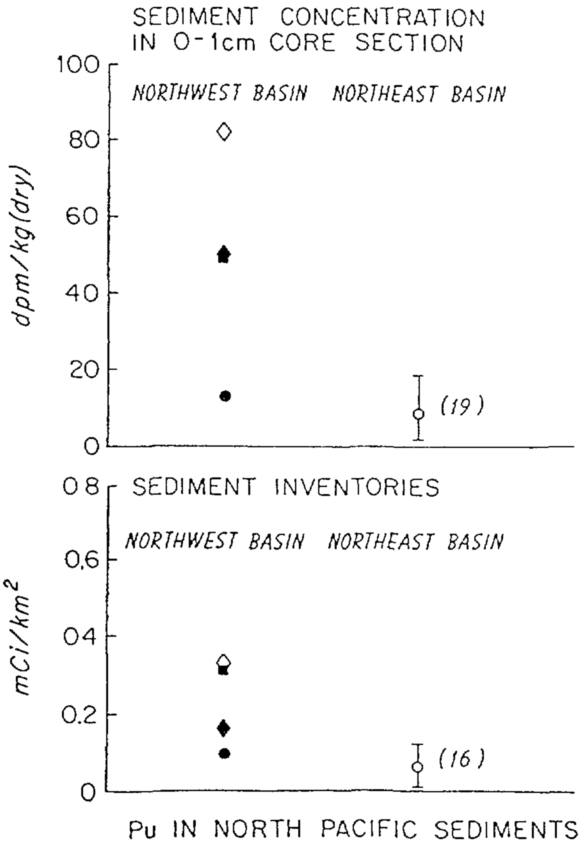

FIGURE 2

It seems necessary, in looking for an explanation of the elevated transuranics in these Western Pacific sediments relative to those from MPG-1, to invoke an extra source of supply associated with input via close-in fallout of debris from tests conducted at the U.S. Pacific test site in the Marshall Islands in the 1950s. This source was necessary to explain the distribution and inventories of Pu in N. Pacific water columns at GEOSECS stations.[1] In the water columns of the Western Pacific in the 30-40° latitude range, Pu inventories exceeded those of the Eastern end of the section by about a factor of 2--the excess Pu being attributed to a close-in fallout source.

Such an input would be expected to be recorded in sediments underlying the input area. Although the necessary data are not available, it seems highly probable that surface seawater concentrations of Pu in the areas affected by close-in fallout from the 1950's test series must have been much higher than those subsequently resulting from fallout from global debris from the stratosphere from the 1960's testing. Euphotic zone scavenging in turn would have supplied underlying sediments with particles transporting substantially elevated concentrations of Pu.

Comparisons of these Pacific sediment Pu inventories with those measured during GEOSECS in the overlying water[1] offers an opportunity to compare, at least qualitatively, the rate of Pu transfer to the deep ocean as a function of whether its source was from close-in or global fallout. It is clear from both the sediment data shown here and the GEOSECS water inventories, that Western N. Pacific stations between 30°N and 40°N must have received proportionately more "close-in" fallout that did those in the Eastern N. Pacific. Specifically the locations represented by the Hakahu Maru cores 2 and 3 have water column plus sediment Pu inventories in the 4.0-4.3 mCi/km^2. range. At the MPG-1 location, the corresponding total is close to 2.9 mCi/km^2. At this latitude, the stratospheric Pu input could well be taken to be about 2 mCi/km^2--as represented by the stations at the eastern end of the GEOSECS E/W section[1] between 30°N and 40°N. When this is subtracted from the total inventories, there is left an estimated inventory of "close-in" fallout of about 2.2 and 0.9 mCi/km^2 at the Hakuho Maru core 2/3 positions and the MPG-1 location respectively. At the former location, Pu is distributed between the ocean water column and the underlying sediments such that about 92% is in the water and about 8% is in the sediments. The corresponding figures for the MPG-1 location are 98% and 2%. If the partition of "close-in" fallout between 160°E and 180°E is put at 2.2 mCi/km^2 in the water and 0.26 mCi/km^2 in the sediments (subtracting the MPG-1 average sediment inventory as being a measure of the stratospheric fallout component), the water/sediments proportions become 11% and 89%. The implication of these comparisons would seem to suggest that the "close-in" fallout Pu was delivered in a form which made it more available to scavenging and particle sinking processes than was stratospherically delivered fallout Pu. An alternative explanation for the higher proportion of fallout Pu found in the 160°E-180°E region sediments compared to the MPG-1 site, would be possible if there were significant differences in the biogenic large particle fluxes between the two areas. Bacon et al.[5] have shown that these fluxes are the major controls on the fluxes of both natural radionuclides and Pu to the deep Sargasso Sea. No comparable particle flux data exist for the two Pacific areas in question, but it is very unlikely that primary productivity differences, and hence biogenic particle fluxes, are sufficiently different to account for the higher proportion of Pu found in 160°E-180°E region sediments compared to that at the MPG-1 site. For these reasons it may be more likely that the observed difference is related to the more reactive character of "close-in" fallout Pu with respect to particle association and sinking.

4.2 Relevance to Radioactive Waste Disposal

There are at least two facets to these data which have relevance to questions associated with the consequences of disposal of radioactive wastes in the oceans.

4.2.1. The elevated Pu concentrations in near surface sediments in areas of the Western N. Pacific means that benthic organisms including infauna have been exposed to levels of transuranics ranging up to an order of magnitude higher than in the MPG-1 study area. This is a favorable situation in respect to determination of benthic organism concentration factors for Pu. These are often hard to measure because of the low level of the fallout signal available. Here, in contrast, levels of organism Pu concentrations should be more rapidly measurable.

4.2.2. Any waste disposal operations which might be planned for the future in the Western Pacific would have to be monitored against the higher fallout background likely to be found there. It makes abundantly clear the necessity of there being an extensive high quality data set on the existing patterns and concentrations of fallout isotopes against which to assess the effects of additional input associated with waste disposal sources.

4.3 Bioturbation Implications of Sediment Plutonium Distributions

The fallout radionuclides and unsupported ^{210}Pb are often used to infer the depth and nature of organism mixing processes in sediments with slow rates of accumulation. In contrast to the relatively deep bioturbational mixing of coastal or shelf sediments,[4,6] deep sea sediment bioturbation is generally thought to be restricted to sediment close to the sediment/water interface. At the MPG-1 site in the North Pacific, for example, fallout nuclide penetration is seldom detectable at depths greater than 10 to 12 cm within the sediment.[2,7]

From the data tabulated in Tables 1 and 2 it is possible to draw some conclusions about the nature and extent of bioturbation in the sediments of the Western North Pacific at the core sites occupied in 1980--Figure 1. At core locations 1-3, the Pu concentration fell below 10% of the upper layer value at a depth 10 cm below the interface. The slope of the concentration curves were generally similar to those seen at the MPG-1 site--implying similar rates of biological mixing. At core location 4, a more intensive mixing rate is implied by the steeper slope of the Pu distribution curve. Also, the Pu concentration at depth does not drop below 10% of the top section concentration until a point somewhere between 15 and 19 cm. This location is characterized by a Pu distribution indicating both greater mixing intensity and to a greater depth within the sediment.

The higher concentrations of Pu found in these sediments compared with those which occur in most other deep ocean sediments, including those at the MPG-1 site, results in the effects of low intensity deep mixing processes becoming detectable if they are active. At locations where ambient concentrations are low, deep section concentrations may fall below the available analytical sensitivity. This point is clearly illustrated in the two high inventory cores (2 and 3). In both cores, Pu is readily measurable in the 20-25 cm depth range--albeit at concentrations 1-2% of their surficial values. Even more striking, in core 3, is the sediment zone between 42 cm and 46 cm where a distinct Pu signal was detectable over that in the overlying and underlying sediment. When this core was extruded, organism burrows were noted as penetrating to this depth.

The surprising conclusion is drawn from these sediment mixing profiles that abyssal sediment mixing activities are not as slow or as shallow as is generally believed. The evidence in these patterns points to the ability of deep ocean organisms to move surficial sediment to considerable depth within the sediment in a relatively short period of time.

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PLUTONIUM DISTRIBUTION IN MARINE AND RIVERINE SEDIMENTS FROM LA SPEZIA AREA (LIGURIAN SEA)

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Abstract

The inventory was 3.5 mCi km^{-2}, much higher than for abyssal sediments. The plutonium concentrations in marine samples (15-71 dpm kg^{-1}) were about ten times higher than for the riverine samples (1.7-4.9 dpm kg^{-1}). Calculations from plutonium distribution in a core suggested a sedimentation rate of 0.56 ± 0.06 cm y^{-1}.

1. Study area

The study area is under the influence of the Magra river which supplies to the sea a limited amount of both water and suspended matter (1) from the drainage of two different basins: above its confluence with the Vara, the Magra flows through a region dominated by marble and dolomite, while the Vara drains a region of sandstone, quartzite and schist. The suspended material coming from the river is transported by the prevailing currents to North West into the La Spezia Gulf(2,3). Riverine surface sediments from the two different basins and marine sediments (6 grab and 1 core samples) (Fig.1) were analyzed for plutonium determination.

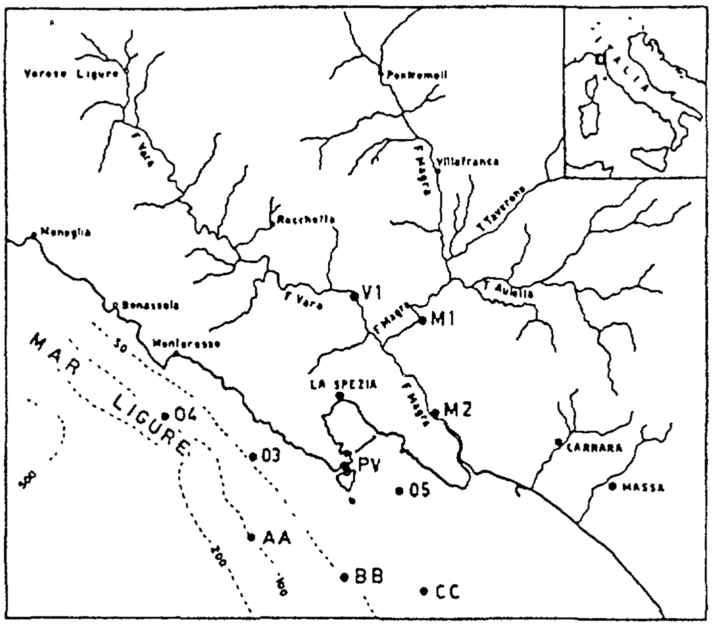

Fig.1 - Study area and sampling points

2. Methods

2.1 Sampling

The marine surface sediments were collected with a Shipeck grab, while the riverine sediments were collected by hand from protected areas. For the evaluation of the vertical distribution of plutonium, a sampling and extruding apparatus was built for the collection of as much as possible undisturbed sediment cores and for the sectioning of the core in slices 1cm high directly in the field.With this procedure it is also possible to discard the outer ring of 1 cm, that can be disturbed by core penetration into the sediment, from each slice.(4)

2.2 Analytical procedure

Among the several published procedures for plutonium separation and purification from the matrix and interferring radionuclides, an extraction procedure much similar to that published by Wong (5) was chosen, but the samples (aliquots of about 15 grams) were totally dissolved by sequential treatment with HNO_3-HF, HCl-H_3BO_3, HNO_3-$HClO_4$. At the end of the dissolution step Pu was isolated from the mixture of acids by coprecipitation with CaC_2O_4, that also provided a preseparation of Pu from the matrix and facilitated the subsequent double anion exchange procedure. The accuracy of the method was tested by analyzing three standard sediment samples from NBS and IAEA. The results are shown in table 1.

TAB. 1: RESULTS OF ANALYSIS OF ^{239,240}Pu IN STANDARDIZED SEDIMENT SAMPLES

SAMPLE	ACCEPTED ACTIVITY (dpm/Kg)	MEASURED ACTIVITY (dpm/Kg)
River sediment NBS SRM 4350B	30.5 ± 1.8	29.4 ± 1.4
IAEA SD-B-2	266 ± 67* 422 ± 44'	351 ± 27
IAEA SD-B-3	1265 ± 155§	1063 ± 19

* Measured at the International Laboratory of Marine Radioactivity (ILMR) by leaching with hydrochloricand nitric acid.

' Measured at ILMR by total dissolution with hydrofluoric, perchloric and nitric acids.

§ Average result from 8 laboratories participating in ILMR intercalibration exercise.

3. Discussion

3.1 Surface sediments

Each sample was measured for porosity and ^{239,240}Pu concentration(Tab.2). The porosities of the river sediments were high (0.62 - 0.79) and representative of the smallest particle

TAB. 2: CONCENTRATIONS OF PLUTONIUM, POROSITIES AND ^{239,240}Pu/^{137}Cs RATIOS IN SURFACE SEDIMENTS OF THE LIGURIAN SEA NEAR LA SPEZIA AND IN ADJACENT RIVER SEDIMENTS COLLECTED IN JULY, 1984. UNCERTAINTIES ARE 1-SIGMA PROPAGATED ERRORS.

Location	^{239,240}Pu (dpm/kg dry)	Pu/Cs **	Porosity	Depth (m)
SP AA	56 ± 3	-----	0.629	100
SP BB	26 ± 2	-----	0.476	47
SP CC	25 ± 2	-----	0.484	24
SP PV	71 ± 4	0.08	0.701	12
SP 03	38 ± 2	0.06	0.588	45
SP 04	60 ± 4	0.07	0.646	93
SP 05	15 ± 1	0.11	nm*	18
Vara River(VI)	4.6 ± 0.6	0.01	0.621	1
Magra River (M1)	1.7 ± 0.5	0.01	0.790	1
Magra River (M2)	4.9 ± 0.5	0.03	0.663	1

* not measured

** ^{239,240}Pu/^{137}Cs. The ^{137}Cs data is from Anselmi et al. (1982) and it is not from the same samples as the Pu data, but from samples collected at the same stations.

TAB. 3: CONCENTRATIONS OF PLUTONIUM AND POROSITIES IN A SEDIMENT CORE RAISED AT PV STATION IN THE GULF OF LA SPEZIA, LIGURIAN SEA, IN OCTOBER, 1983. UNCERTAINTIES ARE 1-SIGMA PROPAGATED ERRORS.

Depth in core (cm)	z' * (cm)	^{239,240}Pu (dpm/kg dry)	Porosity
0-1	0.51	51 ± 2	0.709
2-3	2.8	51 ± 4	0.669
4-5	5.2	52 ± 3	0.655
6-7	7.8	66 ± 3	0.656
7-8	9.1	62 ± 2	0.645
8-9	10.4	75 ± 3	0.641
10-11	13.1	59 ± 2	0.612
12-13	15.7	24 ± 2	0.626
14-15	18.4	20 ± 1	0.644
16-17	21.1	15 ± 1	0.637
19-20	25.1	0.9 ± 0.2	0.636
22-23	29.1	0.8 ± 0.2	0.639
25-26	33.1	0.5 ± 0.2	0.626
30-31	39.8	nd**	0.627

* z' = sediment depth corrected for compaction by the overburden of sediment.

** not detected

sizes exported by the Magra river. Plutonium concentrations in marine sediments were about ten times higher than in river sediments. From literature data on ^{137}Cs concentration in the same study area ^{239,240}Pu/^{137}Cs ratios were calculated in the two cases. The average ratio in the river stations was 0.016, while the average from the marine stations was 0.08, indicating a change in Pu adsorption onto the particles as they contact sea water. Plutonium concentration is highly correlated to porosity, which in turn is related to grain size (6). Porosity and Pu concentration in the range of this study are accurately described by a linear relationship (fig.2).

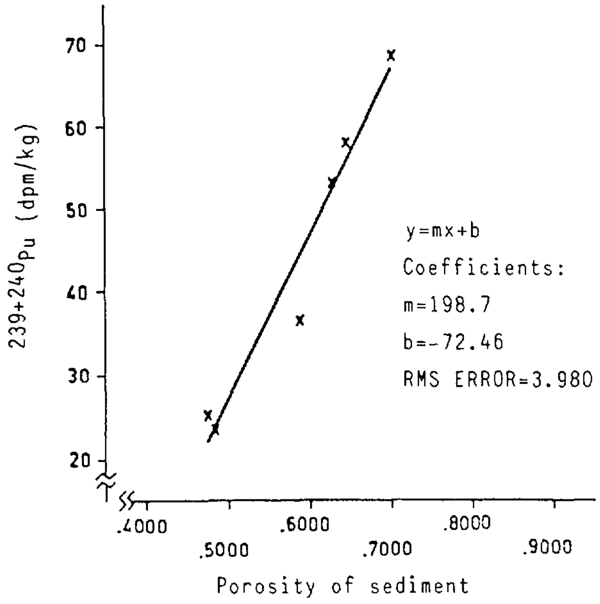

Fig.2 - Relationship between porosity and $^{239+240}$Pu concentration in surface sediments of the Ligurian Sea.

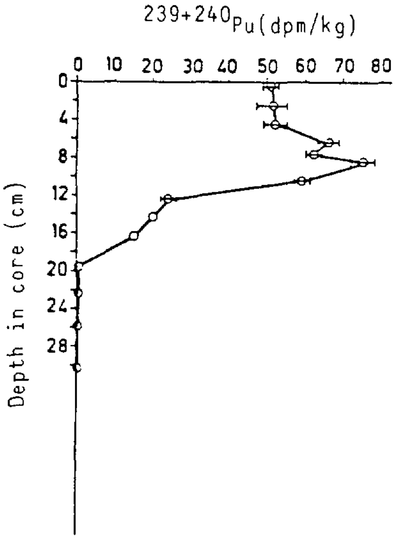

Fig.3 - Vertical profile of $^{239+240}$Pu in sediment core PV collected in october 1983.

3.2 Vertical distribution of Pu - Sedimentation rate

The results of the analyses on the vertical distribution of Pu in the core raised at PV station are shown in Tab.2. The vertical profile (fig.3) shows a well preserved and clearly defined subsurface maximum which suggests that the mixing rate at this station is low as also would be expected from low tidal and wave energy environments.
On the basis of the depth of Pu subsurface maximum, corrected for compaction (7), the average sedimentation rate at this point has been calculated to be 0.56± 0.06 cm/yr.

3.3 Plutonium inventory

The inventory of ^{239,240}Pu in sediments at the coring site was calculated to be 3.5 mCi/km^2, a value which is substantially higher than the cumulative fallout deposition at this latitude, but in good agreement with other published values on coastal Mediterranean (8,9,10) and Pacific sediments (11). These results contrast those in deep water sediments (12,13,14) in which the inventories are only a fraction of that delivered by fallout. The inventory differences between shallow and deep water marine environments may be explaned by the fact that Pu is removed from seawater in primarily hydrous Fe and Mn oxide coatings on particles, both inorganic and biogenic. In the open sea, low particle population and sedimentation regime result in low inventories of Pu in deep water sediments. Zooplankton fecal pellets provide an important transport pathway in this environment. In shallow water, on the other hand, higher primary productivity, greater runoff from land and resuspension of sediments near the sea floor provide greater concentrations of particles and thus enhanced removal of Pu from the water column.

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THE CHEMICAL BEHAVIOR OF LONG-LIVED RADIONUCLIDES IN THE MARINE ENVIRONMENT

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Abstract

Measurements of long-lived radionuclides in the marine environment have provided a wealth of information regarding the physical, biological, and chemical processes which control the behavior of these and many other pollutants in the oceans. Their value as tracers for the dispersion, transport, and fate of pollutants in the oceans is largely dependent on the chemical properties of each individual radioelement. Differences in these properties, particularly in relation to their interaction with biotic or abiotic particulate matter, result in the separation of parent-daughter radioisotopes in the natural radioelement series or in changes in the ratios of fission and activation products. Such differences have provided the means to provide time scales for a variety of transport processes and to determine sedimentation rates. The properties of these radionuclides in the oceans can, in general, be predicted from the chemical properties of the stable elements.

For those elements such a plutonium, for which there are no naturally-occurring stable isotopes, studies of their distribution in the oceans have provided a new important understanding of their chemical behavior. This behavior has not always agreed with what would have been predicted from laboratory studies carried out at far higher concentrations. Differences between observed distributions and laboratory predictions have highlighted the importance of correct experimental conditions in order to avoid confusing experimental artifacts. The interaction of radionuclides with particles in the oceans and marine sediments can be described in terms of simple ion exchange or adsorption equilibria. The magnitude of the effective equilibrium constant for each radionuclide is dependent on the redox properties and complex forming capability of the element in question, the concentration of the stable element, if any, the composition of the water--particularly in relation to the concentrations of complex-forming ligands--and the surface and chemical properties of the particles.

1. INTRODUCTION

Long-lived radionuclides, both natural and artificial, have provided geochemists and oceanographers with a series of extremely valuable tracers. With the advent of nuclear fission several more extremely important radionuclides have become available. Improvements in nuclear radiation measurement technology have provided radiochemists with the capability to measure radionuclides in the marine environment at extremely low concentrations. There are now essentially three sources of long-lived radionuclides in the oceans: (1) natural elements of cosmic origin, e.g. ^{7}Be, ^{10}Be, ^{14}C, ^{26}Al, and ^{32}Si; (2) natural elements of terrigenous origin, e.g. ^{40}K, ^{129}I, and uranium and thorium together with their radioactive progenies and (3) artificial radionuclides, e.g. ^{90}Sr, ^{137}Cs, plutonium (^{238}Pu, $^{239-240}$Pu) and, ^{241}Am.(1)

Measurements of these radionuclides in the marine environment have provided a wealth of information regarding the physical, chemical and biological processes which control the behavior of these and other pollutants in the oceans. The range of these interactive processes is illustrated in Fig. 1. The value of these radionuclides as tracers for processes in the oceans is based largely on differences in their chemical properties, particularly in relation to their apparent solubility or interaction with particles - biotic or abiotic. These differences result in the separation of parent-daughter radionuclides from the uranium or thorium series, or changes in the ratios of fission or activation products for the artificial radionuclides. Since the ratios of introduction of the natural radionuclides to the marine environment (deposition of those of cosmic origin, and <u>in situ</u> production of progeny from uranium and thorium decay) are constant and the deposition of artificial radionuclides, while being extremely variable, is well known(2), both artificial and natural radionuclides may be used, depending on their half-life, as tracers for rate studies of particle movement - vertical or horizontal(1), sedimentation and bioturbation.(3) The differences in the chemical properties of the different daughter products of uranium and thorium provide an effective means to disturb the radioactive equilibria chain and therefore permit the determination of sedimentation rates using ^{230}Th, ^{231}Pa, ^{226}Ra and ^{210}Pb(4), and particle settling rates using ^{234}Th and ^{228}Th.(5) The cosmogenic radionuclides ^{14}C and ^{10}Be have also been used for sediment dating and ^{7}Be to determine particle settling rates.(6)

In addition, because the inputs of the artificial radionuclides have been extremely variable and effectively occurred over a very few years, they can also be used as tracers for rate studies of the mixing of water masses for periods of time governed by their radioactive half-life and mixing times of the oceans.(7)

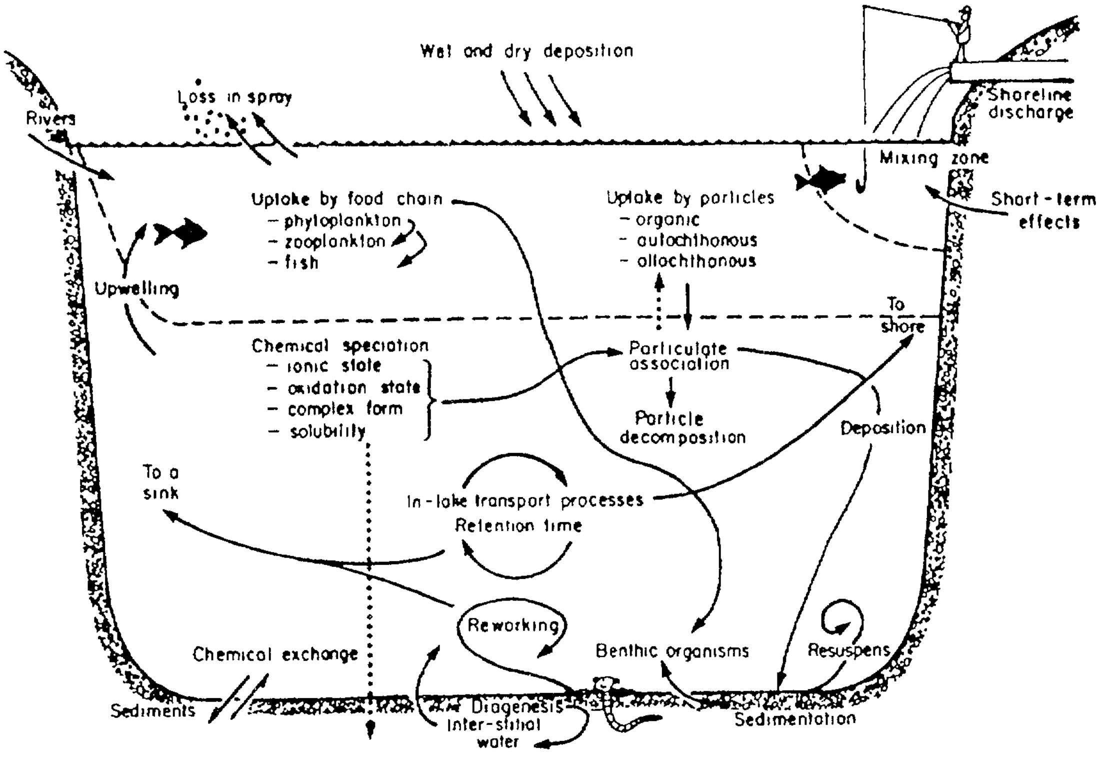

Fig. 1. The physical, chemical and biological interactions of radionuclides in the aquatic environment.

Since thermonuclear testing has also increased the flux of ^{14}C to the oceans, this isotope as well as ^{137}Cs, ^{90}Sr and $^{239-240}Pu$ may also be used in similar studies.

The effectiveness of any radionuclide as a tracer of particles in the oceans will depend on the chemical interactions of the ions or species in solution with a heterogeneous phase - be it a sediment particle or living or dead organisms. It is clear then that a knowledge of the solution chemistry of the ions involved and the surface chemistry of the particles will be critical to the overall understanding of the adsorption process at the water/particle interface.

2. SOLUTION CHEMISTRY

The chemical behavior of ^{137}Cs and ^{90}Sr in solution will be typical of their stable cogeners in Groups I and II. Therefore they will act as tracers for stable Cs and Sr in the water column, will be present, at the pH of seawater, as simple ions, and will participate in exchange reactions with clays. In addition, ^{90}Sr will be intimately involved in carbonate equilibria and substitute for other alkaline earth elements in corals and carbonate shell-materials. Because of the large concentrations of both alkali and alkaline earth elements in the ocean, these two radionuclides will be essentially conservative in the water. However, the decrease in the residence times for the Group I elements in the ocean from 6.8×10^6 years for K^+, to 4.5×10^6 for Rb^+, and to 560,000 years for Cs^+ indicates that there is a preferential removal mechanism for Cs^+ ions onto particles.(8) The residence times for the alkaline earth elements decrease significantly. This is predominantly due to the decrease in the solubility of their sulfates with increasing atomic number.(8)

Of particular importance in this discussion is the behavior of the transuranic elements Np, Pu, Am, and Cm. Since these elements have a far greater tendency to hydrolyze than those in Groups I and II, e.g. ^{137}Cs and ^{90}Sr, they have considerably smaller residence times in the oceans because of their interaction with particles. In addition, several of these elements have more than one oxidation state that can coexist in the environment, and variations in the ratios of oxidation states can exert a major effect on their behavior. While thorium and uranium each occur in the marine environment in a single oxidation state as Th^{4+} - or more likely as hydrolysed species $Th(OH)_n^{(4-n)+}$, and $U^{VI}O_2^{++}$, which tends to act more like a simple divalent ion, both Np and Pu can have several different oxidation states coexisting in solution. However the next two members of the series Am, and Cm apparently occur only in a single oxidation state, Am^{3+} or Cm^{3+}.

Both Np and Pu can coexist under certain circumstances in four oxidation states in acid solution because of the complex relationships involved between the equilibria and the kinetics of conversion from one oxidation state to another. In general, the reactions between M^{3+} and M^{4+}, and $M^VO_2^+$ and $M^VO_2^{++}$ are rapid and those between M^{n+} and MO_2^{m+} are slow. The latter two reactions are clearly dependent on the hydrogen ion concentration. Very different equilibria and kinetics probably pertain at the near-neutral pH of seawater(9,10) than in acid solution where most of the oxidation-state studies have been conducted.

In neutral or basic media the relationships between the oxidation states are less certain because of the difficulties in measuring sensible redox couples at metal concentrations where hydrolysis or precipitation may occur. However, estimates have been made for the formal potentials for plutonium in neutral solution(11)

$$Pu^{3+} \xrightarrow{0.63} \underbrace{Pu(OH)_4yH_2O \; \underline{\;-\;\;1.11\;} \; PuO_2^+ \; \underline{\;-0.77\;} \; PuO_2(OH)_2}_{-0.94v})$$

Under these conditions Pu^{3+} is unstable and Pu^{IV} would appear to be more readily oxidized to Pu(VI) than Pu(V).(10)

Several years ago Nelson and Lovett developed a simple technique to distinguish between Pu(IV) and Pu(V) + Pu(VI) in natural water(12) based on the separation of different oxidation states by co-precipitating with rare earth fluorides as developed by Seaborg.(13) These experiments showed that a large but variable proportion of the plutonium in ocean water is present in the higher oxidation state.

Nelson and Lovett(12) and Nelson et al.(14) have shown that in water samples collected from relatively shallow basins, and near the bottom of the deep ocean, where relatively high suspended particle concentrations are present, the (Pu(V) + Pu(VI)/Pu(IV) ratio is large ~ 5, but in the open ocean the ratio is closer to 1.0. In fresh waters with high dissolved organic carbon concentrations the plutonium is almost exclusively in the Pu(IV) state.(15)

Further experiments by Nelson and Orlandini(16) demonstrated that a laboratory technique developed to separate Np(V) from Np(IV) or (VI) in neutral solution on silica gel where Np(VI) and Np(IV) are strongly, and N_p(V) is weakly adsorbed,(17) could be adapted for use with the very large volumes of water needed to measure the oxidation states of plutonium at environmental concentrations. They have also shown that if a solution of PU(VI) is added to a sample of a natural water, the plutonium is reduced rapidly to Pu(V) unless a holding oxidant like MnO_4^- is present. With no oxidant present the reduction is >90% complete in ~2 hours. Furthermore, using a combination of the techniques outlined above, they have shown that the higher oxidation state of plutonium in natural waters is Pu(V) and not Pu(VI). Measurements by Harvey have shown that neptunium in the Irish Sea is, not unexpectedly, in the Np(V) oxidation state.(18)

The variability in the values of the ratios of Pu(V)/Pu(IV) in different natural waters or in different parts of the oceans raises questions regarding the processes controlling the reactions between Pu(IV) and Pu(V) and the species involved.(19) However, the reaction does appear to be catalyzed or otherwise involve a reaction with particles.

The chemical concentrations of Pu(IV) in ocean waters (~0.2 - 0.5 x 10^{-17} M in the open ocean and up to 3 orders of magnitude greater in the Irish Sea(20) are far greater than one would predict for the solubility of Pu^{4+} in equilibrium with solid $Pu(OH)_4$ at pH8 ($\approx 10^{-32}$M, K_{So} = 10^{56})(21) In contrast, since $Pu^{V}O_2^+$ behaves essentially as a univalent ion, it is very soluble in water with a solubility product K_{Sp} = $10^{-8.6}$, and its maximum concentration at pH 8 could be as high as 2.5 x ~10^{-3} M before precipitation is likely to occur. Since up to 20% of the Pu is present as Pu(IV), the observed concentrations of Pu(IV) must be a result of complexing by ligands which are readily available in natural waters. Pu(IV) forms strong complexes with a variety of inorganic and organic ligands which are known to stabilize this oxidation state in solution. In particular it has been shown that 5 x 10^{-4} M citrate ion solution prevented the formation of Pu(IV) hydroxide polymer in a solution with $[Pu]_t$ = 10^{-5} M at pH values as high as 11.(13)

3. INTERACTION WITH SEDIMENTS

It is foolhardy to believe that it will be possible to understand the behavior of radionuclides in the oceans solely in terms of their solution chemistry. The interaction of ions with particles in the water and in the sediments will modify their behavior and perhaps exert the major control on their transport and fate in the environment.

Detailed studies of the behavior of plutonium, and other radionuclides in restricted bodies of water have provided a great deal of information on their association with particles and transfer to the sediments.(22,23) Measurements of the distribution of radioactivity associated with different geochemically defined phases - such as specific minerals or surface coatings - have provided information on the chemical nature of the interaction at the particle-water interface.(23) Changes in these distributions within the sediment column can provide insight into possible differences in behavior due to diagenetic reactions involving changes in the concentration of ligands or redox conditions.(19,24) A great variety of chemical techniques have been utilized to develop a sensible scheme to assess the geochemical association of elements with particles (in particular, that part not found in sediments deposited in predevelopment times). The different schemes have been reviewed elsewhere.(25) The basic classification of Gibbs identified four types of association - ion-exchange, adsorption with iron, manganese and other hydrous oxides, complexation by surface organic molecules, and incorporation into a crystalline or residual fraction.(26) However, Edgington has shown that such a simple classification apparently breaks down for ^{210}Pb, since a large fraction of the total loading is apparently in the residual fraction - an observation that is difficult to reconcile since almost all of the ^{210}Pb is of very recent origin (via the atmosphere) and readily removed from sediment by dilute acid.(27)

While clay minerals are generally the major component of the fine grain sediments which may adsorb trace metals or organics in the ocean, their residual surface charge permits the formation of organic or hydrous oxide surface layers which can drastically modify these adsorption properties at the surface. The hydrous oxides and in particular, hydrous ferric oxide surface layers are ubiquitous, adsorb many trace metals and have been the subject of intense study.(28) Thus it is not surprising to find that the extraction results for plutonium and americium on sediments from the Great Lakes and Buzzards Bay show that these elements are associated almost entirely with the reducible hydrous oxides, and that this association does not change with depth, and presumable redox conditions, in the sediments.(23,29) Aston has found a similar result for sediments from the Irish Sea.(30)

At this point it is clear that the behavior of the radionuclides in the oceans is very dependent on not only their solution chemistry, but also the surface chemical properties of the adsorbing solids. Using plutonium as an example, because of its importance and occurrence in multiple oxidation states, a simple equilibrium model can be proposed to describe the interaction of this element with particles in the ocean. This is illustrated in Fig. 2. The model involves five different chemical reactions or equilibria:

(1) <u>The oxidation/reduction couple Pu^{IV}/Pu^{V}</u>

$$Pu^{4+} + 2H_2O \rightleftharpoons PuO_2^{+} + 4H^{+} + e \qquad (3.1)$$

$$K_{IV,V} = \frac{[PuO_2^{+}]\,[H^{+}]^4}{[Pu^{4+}]} \qquad (3.2)$$

The studies of Nelson and Lovett(12) and Nelson and Orlandini(16) have shown that there are great differences in the values of the ratio of Pu(V)/Pu(IV) in ocean water. In the Irish Sea the ratio is strongly in favor of the oxidized state, ≃ 0.8, but in the Pacific Ocean the ratio decreases to ~ 0.5, but in water just above the sediment/water interface rises to ~ 0.8. Unpublished data from Nelson shows that the ratio also decreases with increasing distance north from the Irish Sea and around the north of Scotland.(31). Laboratory studies have shown that in separate samples of carefully filtered Lake Michigan water, Pu(V) and Pu(IV) are stable, but in the presence of ~ 1 $mg \cdot l^{-1}$ of sediment particles the Pu(IV) is rapidly oxidized and the Pu(V) is rapidly

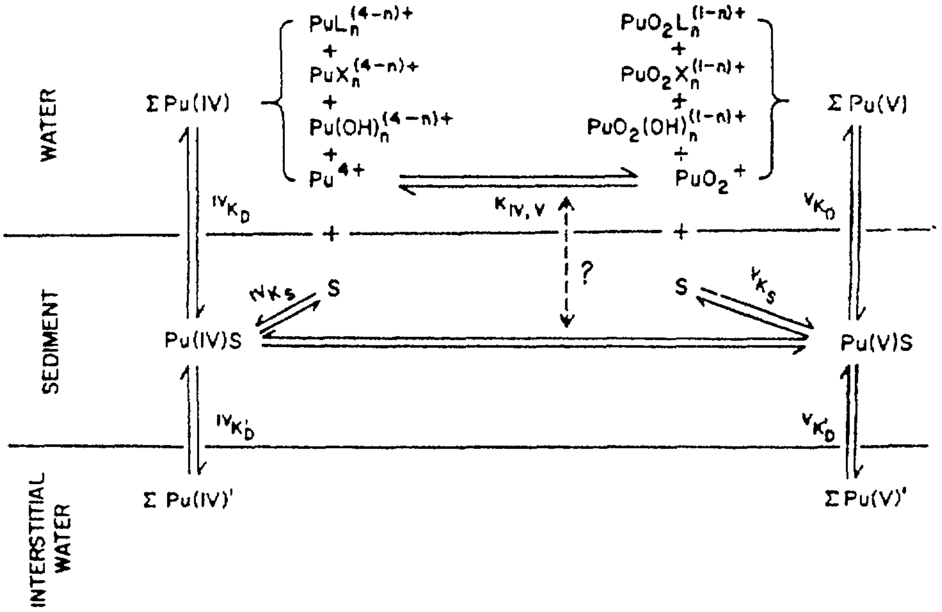

Fig. 2. The role of hydrolysis and complex formation reactions in the interaction of plutonium or other actinides with sediments and their relation to measured values of K_D.

reduced to the extent that the Pu(V)/Pu(IV) ratio ≃ 0.8, the ambient ratio measured in Lake Michigan water.(16) Thus it appears that the redox reaction is catalyzed by the presence of terrigenous particles.

(2) The Hydrolysis of Pu^{4+} and PuO_2^+

The study of the hydrolysis of Pu^{4+} has been hampered by the formation of colloidal species at fairly low pH values, and the maximum concentration of Pu^{4+} ions in solution is limited by the solubility of $Pu(OH)_4$:

$$K_{S_o} = [Pu^{4+}][OH^-]^4 = 10^{-56} \qquad (3.3)$$

The hydrolysis of Pu^{4+} however proceeds in a stepwise manner:

$$Pu^{4+} + H_2O \rightleftharpoons Pu(OH)^{3+} + H^+ \qquad (3.4)$$

$$PuOH^{3+} + H_2O \rightleftharpoons Pu(OH)^{2+} + H^+ \quad \text{etc} \qquad (3.5)$$

with the possible formation of anionic hydroxyl complexes with formation constants:

$$Pu(OH)_4 + OH^- \rightleftharpoons Pu(OH)_5^-$$

$$*K_1^H = \frac{[PuOH^{3+}][H^+]}{[Pu^{4+}]} \qquad (3.6)$$

$$*K_2^H = \frac{[Pu(OH)_2^{2+}][H^+]}{[PuOH^{3+}]} \quad \text{when } *\beta_2^H = *K_1^H *K_2^H \qquad (3.7)$$

$$\vdots$$

$$*K_5^H = \frac{[Pu(OH)_5^-][H^+]}{[Pu(OH)_4]}$$

where ${}^{*}\beta_5^H = {}^{*}K_1^H \cdot {}^{*}K_2^H \cdot \ldots \cdot {}^{*}K_5^H$

The values of the formation constants for the hydroxyl complexes of Pu^{4+} are subject to some speculation. The values reported for $\log {}_{*}K_1^H$ for Pu^{4+} are almost identical to those for U^{4+}, $\log {}_{*}K_1^H \simeq -1.6$.(21) More recently, Allard has critically examined the solubilities of the actinide elements in neutral or basic solutions and quotes values for $\log\ {}_n^H$ (n = 1 to 5) based on the solubility of U^{4+}.(9) The ratios of $\frac{[Pu(OH)_n^{(4-n)+}]}{[Pu^{4+}]} = \frac{{}^{*}\ {}_n^H}{[H^+]^n}$ and the maximum $[Pu(OH)_n^{(4-n)+}]$ concentrations in equilibrium with $Pu(OH)_4$ at pH 8 and thus $[Pu^{4+}]^n (\simeq 10^{-32})$ at pH 8 are shown in Table I.

Table I. Hydrolysis of Pu^{4+}. Stability Constants and Relative Concentrations of the Principal Monomeric Hydrolysis Products.

n	1	2	3	4	5	
$\log {}_{*}B_n^H$	-0.5	-2.5	-6.0	-11.5	-20.0	
$\frac{[Pu(OH)_n^{(4-n)+}]}{[Pu^{4+}]}$	3.2×10^{7}	3.2×10^{13}	1.0×10^{18}	3.2×10^{20}	1.0×10^{20}	
$[Pu(OH)_n^{(4-n)+}]^a$	3.2×10^{-25}	3.2×10^{-19}	1.0×10^{-16}	3.1×10^{-12}	1.0×10^{-12}	<u>M</u>

^{a}Calculated maximum concentrations in equilibrium with $Pu(OH)_4$, $\log K_{S0} = -56.0$

Values of $\log {}^{*}\ {}_n^H$ taken from ref (9).

If the estimates of these formation constants are correct then concentrations of plutonium up to ~4 x 10^{-12} <u>M</u> in natural water at pH 8 in equilibrium with $Pu(OH)_4$ can be explained completely in terms of complexing by the hydroxyl ion.

In contrast, at the concentrations of plutonium (V) likely to be encountered in the ocean, the dominant species will be $Pu^{V}O_2^{+}$, since univalent ions do not readily hydrolyse or form complexes.

(3) <u>Complex Formation (Inorganic HX, or Organic HL), Ligands</u>

Pu(IV) and Pu(VI) hydroxides will also dissolve in carbonate solutions to form complexes.(32,33) The estimates of the stability-constant for the Pu(IV)-carbonate complex, based on solubility measurements, $K \simeq 10^{46}$, appears to be rather high in comparison with values for comparable ligands such as citrate ${}_{*}K \simeq 10^{25}$ or oxalic acid $K_1 = 10^{8.7}$.(21) It has been suggested that carbonate anionic complexes could be the major species in solution. Such a hypothesis was attractive before it was discovered that the predominant upper oxidation state in solution was Pu(V) rather than Pu(VI), since U(VI), the analogue for Pu(VI) is present in seawater as an anionic carbonate complex, $UO_2(CO_3)_3^{4-}$.(34)

Even though Pu^{4+} forms relatively strong complexes with SO_4^{2-} ion, e.g.

$$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+ \qquad {}_*K_1 = \frac{[PuSO_4^{2+}][H^+]}{[Pu^{4+}][HSO_4^-]} \tag{3.8}$$

where ${}_*K_1 = 740$,(22) the $[SO_4^=]$ in seawater is only 3×10^{-2}M, which is not great enough to contribute a significant fraction of the total Pu^{IV} in solution in the oceans.

In a discussion of complexing in solution, the formation of organic complexes cannot be ignored. The importance of humic acids as principal complexing agents in natural waters and sediments is well established.(35) While it appears that complexation by the hydroxyl ion could account for the observed concentration of Pu(IV) in water, the potential role of complexing by humic acids should be addressed. Unfortunately there are no directly measured values of a stability constant of Pu(IV) (or any similar element) with humic acids.

However, Nelson _et al_. have shown that additions of humic acid (soluble organic carbon) to natural waters significantly depress the adsorption of plutonium onto autosediments suggesting the formation of complexes and this permits the calculation of conditional stability constants(36).

(4) Interaction with Sediment.

The interactions of metal ions with sediments that have been discussed earlier in this paper can be expressed in terms of a simple heterogeneous chemical reaction analogous to reactions with complexing ligands. For simplicity it will be assumed that the only ionic species interacting with the hydrous iron oxides is Pu^{4+} (however this could be a hydroxo complex, see Hsi and Langmuir(37):

$$Pu^{4+} + HS_{sed} \rightleftharpoons Pu^{IV}S_{sed} + H^+ \tag{3.9}$$

and

$$^{IV}K_S = \frac{\{Pu(IV)S\}[H^+]}{[Pu^{4+}]\ \{HS\}} \tag{3.10}$$

where [ ] = moles$\cdot$l^{-1} and { } = moles$\cdot$kg^{-1}

There are two major problems in using this equilibrium reaction. The first is the parameterization of {HS}, which is essentially the concentration of active exchangeable sites on the sediment particles. However, several techniques have been developed to estimate {HS}.(38) The second problem is that the reaction with sediment particles may be more complex than illustrated here. James and Healy have suggested that metal hydroxo species are more strongly adsorbed than free metal ions since the adsorption of metals is strongly pH-dependent.(39) Other models have been developed which explain the pH-dependence in terms of the activity of the $\equiv Fe - O^-$ groups.(28)

(5) The Distribution Coefficient, K_D

Since it is impossible to measure the concentration of each plutonium species in solution the association of plutonium with sediments is expressed in terms of a distribution coefficient, (a parameter commonly used in describing heterogeneous equilibrium in solvent extraction and ion exchange).

$$K_D = \frac{\text{Total Pu}\cdot g^{-1}\text{ sediment}}{\text{Total Pu}\cdot ml^{-1}\text{ in solution}} \tag{3.11}$$

$$= \frac{\{Pu^{IV}S\} + \{Pu^{V}S\}}{[Pu(IV)] + [Pu(V)]} \qquad (3.12)$$

where

$$[Pu(IV)] = [Pu^{4+}] + {}_n[Pu(OH)_n{}^{(4n)+} + {}_n[PuX_n]^{(4-n)+} + {}_n[PuL_n{}^{(4-n)}] \qquad (3.13)$$

and also ${}^{IV}K_D = \{Pu^{IV}S\}/[Pu(IV)]$ and ${}^{V}K_D = \{Pu^{V}S\}/[Pu(V)]$.* The definition of these equilibrium constants ${}^{IV}K_D$ and ${}^{V}K_D$ for the interaction of plutonium with sediments presumes that these reactions are reversible. A large proportion of the measured values of K_D, which ipso facto are assumed to be the equilibrium constants, have only been measured for the uptake reaction. Edgington et al. have studied the uptake and desorption of plutonium on sediment and have shown that the same K_D values for Pu(IV) and Pu(V) can be obtained from uptake and desorption studies when approaching the equilibrium from either side.(41) The oxidation states of plutonium on sediment particles have been determined using a mild leaching technique. The results show that the plutonium on particles is almost entirely in the Pu(IV) oxidation state, and that very little Pu(V) is found.(12) However, the value of ${}^{V}K_D$ estimated from these experiments, ≤ 1000 is in close agreement with the value measured by Harvey for Np(V), ~250, in the laboratory.(18) The value of the K_D measured for Np in the Irish Sea is greater than that for Np(V) measured in the laboratory, but far less than the value of either ${}^{IV}K_D$ (Np) measured also in the laboratory or the value of the overall K_D for plutonium measured in the Irish Sea.(18) These data suggest that there is less reduction of Np(V) than Pu(V) in the Irish Sea and that $K_{IV,V}$ (Np) << $K_{IV,V}$ (Pu)(see equa. 3.2).

A large number of K_D values have been measured for the transuranic elements: representative values for these, as well as for Th, and U for comparison, are summarized in Table II. The magnitude of the measured K_D's vary in the order:

$$K_D[Th(IV)] \cong K_DpPu(IV)] \cong K_D[Am(III)] >> K_D[U(VI)] > K_D[Np(V)] \cong K_D\ [Pu(V)]$$

Table II. Comparison of the Values of the Distribution Coefficients (log K_D) for the Actinide Elements from Field and Laboratory Measurements

Element	Field	Laboratory
Th(IV)	6.9(49) - > 7.0(42)a	---
U(VI)	3.0(43) - 3.90(42)a	---
Np(IV)	----	4.30(18)
Np(V)	3.70(18)b	2.40(18)
Pu(IV)	6.40(14,19)	5.70 - 6.40
Pu(V)	$\leq$3.00(14)	
AM(III)	6.08(44)	5.40 - 5.70(45)
Cm(III)	6.09(44)	

[a] These values may not reflect a true K_D since no attempt was made to determine whether all of the Th or U in the bulk sediment was involved in the surface exchange reaction.

[b] Since no separation of Np(V) and Np(IV) was made for the sediment this value probably reflects a contribution from Np(IV) adsorbed to the surface.

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*A similar parameterization involving complexation has been suggested recently to account for variations in the distribution coefficients for hydrophobic organic molecules between natural waters and sediments. The authors suggest organic-organic interactions in the aqueous phase(40).

Considering the wide variety of sediment types involved, possible differences in the particle-size distribution of the sediments examined, and the variation in the ratio of oxidation states, it was encouraging to find that the reported values for K_D(Pu) for oceanic sediments have a relatively small range.(19) Duursma and Bosch have shown that variations of a factor of 5-10 in the value of K_D can be explained solely by differences in the particle-size distribution in natural sediments.(46) In those cases where the values of K_D are the greatest, the sampling technique favored the collection of extremely fine-grained sediments, as has been discussed elsewhere.(19)

There are some differences between the values of K_D measured in the field and the laboratory. These differences can arise from perhaps two major causes which are related to experimental conditions. First and foremost there is the question of particle size alluded to above. Values of K_D measured on bulk sediment in the laboratory would be expected to be lower than those values calculated from the analysis of suspended sediments. Secondly, a factor, particularly important when discussing the behavior of plutonium, is the question of the ratio of oxidation states and the chemical form of the radionuclide used for the measurements. As the [Pu(V)]/[Pu(IV)] ratio decreases, the value of the measured K_D will increase. Secondary factors could be related to the effect of variations in the composition of the water or sediment used, related to changes in the concentration of potential complexing agents in the water, sediment, or sediment/water ratio. The depression in the value of K_D for plutonium in the interstitial water of Irish Sea sediments is presumably due to an increased concentration of organic complexing agents due to the diagenesis of natural organic material in the interstitial water(47) as are the observations by Santschi et al. that the K_D for americium is depressed considerably when the sediment/water ratio is increased.(45)

The definition of K_D implies that the total concentration of metal adsorbed is a linear function of the concentration in solution. This definition is only true as long as the fraction of the exchanageable sites occupied by metals remains relatively small. When the surface coverage becomes significant, deviations from linearity are common and the Langmuir or Freundlich isotherms must be employed. However, for the transuranic elements, the probability of having total concentrations present in the oceans, such that K_D ceases to be constant, is unlikely.

Care must be taken that K_D values are reported for conditions that closely approximate natural conditions, or that both the solid and solution phases are well characterized so that extrapolations are valid. Recently Webber *et al*. have shown that the decrease in K_D of hydrophobic organic compound with increasing solid/water ratio is accompanied by a change in turbidity in the aqueous phase(48) and this can be interpreted in terms of the formation of organic-organic association.(40)

4. EFFECT OF ELEVATED CONCENTRATIONS OF PLUTONIUM

The problem of the hydrolysis of Pu^{4+} in even moderately strong acid has plagued chemists since this element was first produced by man. Plutonium polymers appear as soon as a solution of Pu^{4+} in acid was diluted by adding water. Even though the overall acidity in solution was ~1 M, local areas of very high pH are formed causing the colloid to form. Nelson et al., as part of a study to determine the true solubility of plutonium in water, have developed techniques to prepare stable, relatively concentrated solutions of Pu^{4+} and PuO_2^+ for use in this and other environmental studies.(49) Solutions containing PuO_2^+ are made simply by adding solutions of Pu^{VI} in dilute nitric acid to the lake or ocean water - reduction of Pu^{VI} to Pu^V is rapid and complete. Solutions containing Pu^{4+} are prepared by evaporating a solution of Pu^{4+} in 8m HNO_3 to dryness and dissolving the residue in a 1 M $NaHCO_3$ solution.

Using solutions prepared in this manner Nelson et al. have shown, by adding successively higher concentrations of plutonium to Lake Michigan water containing suspended sediment, that the apparent constants established at in the field at 10^{-17} -- 10^{-18} M for the Pu(V)/PU(IV) ratio - 5 and the ${}^{IV}K_D$ ~ 5 x 10^5 do not change over a concentration range of a factor of ~10^{10}. At a total plutonium concentration in solution between 10^{-6} and 10^{-7} M, the value of ${}^{IV}K_D$ increased dramatically indicating the formation of an insoluble hydroxide resulting from the exhaustion of the complexing capacity of the ligands in the water and/or the saturation of adsorption sites on the sediments.

5. EVALUATION EQUILIBRIUM CONSTANTS FOR A MODEL SYSTEM

The observation by Nelson et al. that there is a linear increase in [PuIV] in solution with increasing total concentration of plutonium over ~10 orders of magnitude, indicating a constant value of K_D, and a constant ratio of [Pu(V)]/[Pu(IV)] states provides a means to evaluate a limiting-value for {HS}, the concentration of active exchangeable sites on sediments.

Synthetically prepared goethite and FeOOH have been shown to have a total number of exchange sites ~ 1 - 1.35 moles·kg^{-1}, but ocean surface sediments have in excess of 2.7 moles·kg^{-1} as determined by tritium exchange.(38) In this sediment the exchange sites included all hydrous oxides and not iron oxides in particular. Numerous workers have shown that transition metals, unlike plutonium or americium, are not solely associated with reducible hydrous oxides(25), and that the value of K_D starts to decrease when the ratio of {MS}/{HS}, the fractional surface coverage, exceeds 0.1 - 0.2.(38) In fact, Eddington has shown that only ~ 30% of ^{210}Pb is associated with this phase.(27) In the case of the Lake Michigan sediment, a direct determination of the number of exchange sites has not been determined, and a value based on the measured concentration of readily extractable iron will be used, because plutonium and americium do appear to be specifically bound to reducible oxides.(23) The fine-grained Lake Michigan sediments contain ~ 3-4% total iron, and the concentration of iron that is released with other hydrous oxides by reduction and extraction using the citrate-dithionite method is ~ 15 mg g^{-1} or ~ 0.25 moles·kg^{-1}.(27)

Provided that the required surface sites are available in excess and the K_D is independent of the total metal concentration, an adsorption equilibrium constant may be calculated for the reaction, eqn (3.9)

$$Pu^{4+} + HS \rightleftharpoons Pu^{IV}S + H^+$$

where, from eqn (3.10)

$${}^{IV}K_S[H^+] = \{Pu^{IV}S\}/[Pu^{4+}]\{HS\}$$

Other workers express the constant in terms of the total metal concentration in solution and thus(37):

$$\text{e.g.} \qquad {}^{IV}K_S = \frac{{}^{IV}K_D[H^+]}{\{HS\}} \qquad (5.1)$$

Now if the maximum concentration of Pu(IV) that can be held in solution in a natural water, e.g. Lake Michigan, can be increased to ~ 10^{-8} M without any apparent change in the value of K_D, the fractional surface coverage can have a value where $\{MS\}/\{HS\} \leq 0.01 - 0.02$. Thus for a $K_D = 5 \times 10^5$, at [Pu IV] = 10^{-8} M, the maximum value of {Pu(IV)S} is 0.005. If the value of {Pu(IV)S}/{HS} is not to exceed 0.01 - 0.02, and the minimum value of {HS} $\simeq$ 0.25 M, assuming all of the citrate-dithionite extractable iron must be on surface as exchange sites. While it is now possible to calculate a value of ${}^{IV}K_S$, having established reasonable values of [Pu^{4+}], {Pu(IV)S}, and {HS}, there still remains a question as to whether a single species is adsorbed e.g. Pu^{4+}, or whether other species are adsorbed as well, Pu(OH)$^{3+}$, Pu(OH)$_2^{2+}$ etc. Under such conditions ${}^{IV}K_S$ may be defined e.g.

$$^{IV}K_S = \frac{\{Pu^{IV}S\}[H^+]}{[Pu^{4+}]\{HS\}} \quad , \quad ^{IV}K_S = \frac{\{Pu(OH)_2S\}[H^+]}{[Pu(OH)_2{}^{2+}]\{HS\}} \quad \text{etc.}$$

Balistrieri and Murray avoid the problem of defining the exact species in solution by defining the constant in terms of the total metal concentration in water(37)

$$K_S = \frac{\{MS\}[H^+]}{[M]_T\{HS\}} = \frac{K_D[H^+]}{\{HS\}} \tag{5.2}$$

For plutonium a value of $^{IV}K_S$ may be defined in this manner as

$$^{IV}K_S = (5 \times 10^5) \times (10^{-8}) = 2 \times 10^{-2} \text{ or } \log {}^{IV}K_S = -1.7.$$

The definition of the constants in this manner normalizes the observed values of K_D for sediments with widely differing concentrations of exchange sites, and allows a direct method of comparison for the complexing strength of metals with other sediments. Balistrieri and Murray report values of log K_S for Cd, Cu and zinc in geothite of 0, -1.3 and -3.2, respectively, and for zinc onto a fine-grain sediment, a value of -0.6.(38) The K_D value for Am(IV) on the same sediment is ~ 10^6, log K_S = -1.4.

6. COMPLEXING BY NATURAL ORGANIC COLLOIDS

In an elegant series of experiments Nelson et al. have investigated the complexing effects of natural organic macromolecules (humic acids) on the adsorption of plutonium and americium to sediment particles.(36). The complexing ability appears to be a function of the source of natural dissolved organic carbon (D.O.C.). The effect on the value of $^{IV}K_D$ of readding increasing concentrations of D.O.C. (concentrated from Lake Michigan water by dialysis, M.W. cut off 1000) into depleted Lake Michigan is shown in Fig. 3. Up to the normal concentration of D.O.C. in Lake Michigan water (≃ 1 $mg \cdot l^{-1}$) the value of $^{IV}K_D$ remains essentially constant. As the concentration is increased to values >3.0 $mg \cdot l^{-1}$ the value of $^{IV}K_D$ decreases markedly, the slope of the plot of log $1/K_D$ vs log D.O.C. increasing rapidly to a value approaching 2, suggesting that a mixture of PuL and PuL_2 complexes are formed.

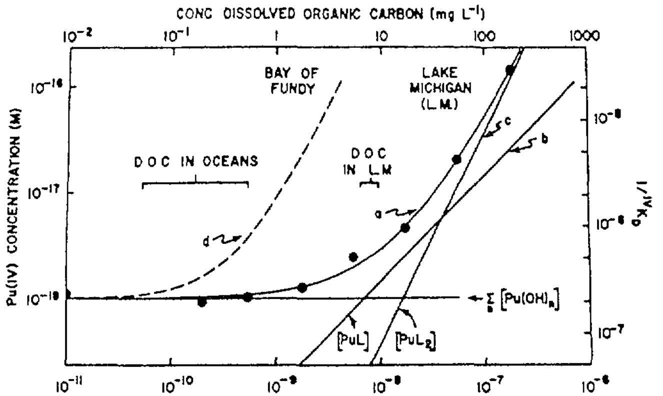

Fig. 3. Comparison of the observed and calculated effect of increasing the concentration of colloidal D.O.C. on the value of $^{IV}K_D$ for plutonium in natural waters.

(a) Observed data for Lake Michigan water and best fit calculated from eqn. 6.6 with $_*\log {}_*K_1{}^L = 20.7$ and $\log {}_*K_2{}^L = 0.7$,

(b) concentration of PuL^{3+},

(c) concentration of $PuL_2{}^{2+}$,

(d) calculated change in K_D for ocean water from the Bay of Fundy using the constants given by Nelson et al.(51)

Starting with the definition of K_D given above, it is clear that since concentrations of D.O.C. less than the present concentration in Lake Michigan do not change the measured value of ${}^{IV}K_D$ significantly, then at D.O.C. concentrations $\leq 2 - 3$ mg·l^{-1}, using the same form as in equ (3.16), but for Pu(IV) only,

$$ {}^{IV}K_D = \frac{\{Pu^{IV}S\}}{[Pu^{4+}] + {}_n[Pu(OH)_n] + {}_n[PuX_n]} \tag{6.1}$$

where X represents any inorganic complexes present,

$$\text{or} \quad {}^{IV}K_D = \frac{K_S^*}{1 + {}_{n*}K_n{}^H[OH]^n + {}_{n*}K_n{}^X[X]^n/[H^+]^n} \tag{6.2}$$

where $K_S^* = {}^{IV}K_S\{HS\}/[H^+]$.

Similarly if the concentration of dissolved organic carabon is [HL], and 1:1 and 1:2 complexes are formed, the value of the distribution coefficient will decrease to:

$$ {}^{IV}K_D = \frac{K_S^*}{1 + {}_{n*}K_n{}^H[H^+]^{-n} + {}_{n*}K_n{}^X[X]^n[H^+]^n + {}_*K_1{}^L[HL][H^+]^{-1} + {}_*K_1{}^L{}_*K_2{}^L[HL]^2[H^+]^{-2}}$$

Inverting this expression and substituting for ${}^{IV}K_D$ leads to

$$ \frac{1}{{}^{IV}K_D} = \frac{1}{{}^{IV}K_D} + \frac{{}_*K_1[HL][H^+]^{-1}}{K_S^*} + \frac{{}_*K_1{}_*K_2[HL]^2[H^+]^{-2}}{{}^{IV}K_S} \tag{6.4}$$

Nelson et al. have studied the effects of increasing the concentration of D.O.C. on ${}^{IV}K_D$ for several different natural waters - both fresh and marine - and have found that while most waters collected in the northern United States behave somewhat similarly to Lake Michigan (Fig. 4) in that they form both 1:1 and 1:2 complexes, fresh and marine waters from the southern states form 1:1 complexes only.(36) They found that the values of ${}_*K_1{}^L/K_{S*}$ giving the best fit to data varied by a factor of 100 - from 9.7×10^{-5} in a southern swamp to 7.5×10^{-7} in Lake Michigan. Ocean waters from the Gulf of Mexico (1:1 complex only) and Bay of Fundy (1:1 and 1:2 complexes) had values of 4.0×10^{-6} and 8.8×10^{-6} respectively.

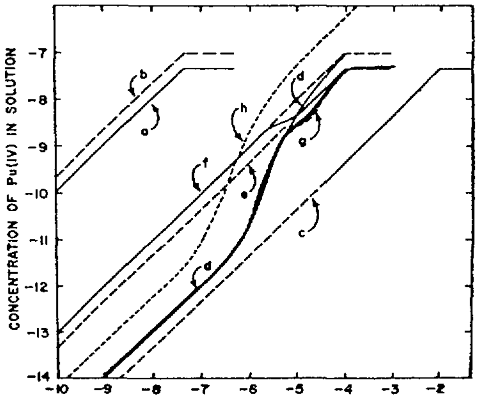

Fig. 4.

Schematic representation of the predicted variation in the concentration of plutonium in solution, [Pu(IV)], as a function of total plutonium added to the system.

(a) No sediment, complexing by hydroxl ion only;

(b) effect of additional complexing by naturally occurring ligands;

(c) - 0.1 g.sediment l^{-1}, ${}^{IV}K_D = 5 \times 10^5$;

(d) the effect of exceeding the adsorption capacity of the sediment, *${}^{IV}K_D$ decreases by factor of 100;*

(e) same as (c) with ${}^{IV}K_D = 5 \times 10^3$;

(f) the effect of exceeding the complexing capacity of the natural ligands;

(g) the effect of exceeding both the adsorption and ligand complexing capacities of the system;

(h) the variation in [Pu(V)] under same conditions as (d).

From the data shown in Fig. 3 it is possible to estimate values of $_*K_1{}^L$ and $_*B_2{}^L$. The total [Pu(IV)] in solution in Lake Michigan (which is $1/{}^{IV}K_D$ is given by the denominator of equation (6.3)

$$1/({}^{IV}K_D) \quad [Pu(IV)] \quad (1 + {}_{n*}B_n{}^H[H^+]^{-n} + {}_*K_1{}^L[HL][H^+]^{-1} + B_2{}^L[HL]^2[H^+]^{-2}) \quad (6.5)$$

From the experimental data shown in Fig. 3 it is evident that complexing by a component of the dissolved carbon contributes a measurable fraction (~ 25%) of the total [Pu(IV)] found in the water. The data also indicate that the change in K_D is due to the formation of 1:1 and 2:1 complexes. Since the only change made to the system in these experiments is to increase the concentration of [HL] + [L^-], then

$$1/({}^{IV}K_D)\ (1/({}^{IV}K_D) = {}_*K_1{}^L[HL][H^+]^{-1} + {}_*B_2{}^L[HL]^2[H^+]^{-2} \quad (6.6)$$

The ratio of the value of the ratio of $_*K_1{}^L/{}_*B_2{}^L$ giving the best fit to the data was found to be ~ 5.0. Using the same assumptions made earlier $_*K_1{}^L = 5 \times 10^{20}$ and $_*B_2{}^L = 1 \times 10^{20}$ or $_*K_2{}^L = 0.2$. The variations in the concentrations of the PuL and PuL_2 complexes alone are also shown in Fig. 3. At the concentration of colloidal D.O.C. in Lake Michigan water (~ 1 mg·l^{-1}), the increase in concentration of Pu(IV) is solely due to the formation of PuL. The concentration of D.O.C. would have to increase by a factor of ~ 10 before the concentration of the [PuL_2] became significant.

The conditional stability constants ($_*K_1{}^L$) for the humic acid complexes in the marine environment vary between 2.7×10^{21} for the Gulf of Mexico and 5.8×10^{21} for the Bay of Fundy. Considering that the concentration of D.O.C. in ocean water is ≤ 0.3 of the concentration in Lake Michigan, it is still apparent that complexing by humic acids could be very important at certain locations in the marine environment. Also shown in Fig. 3 is the calculated change in concentration of Pu(IV) for water in the Bay of Fundy based on the constants given by Nelson et al.(36) If the concentration of D.O.C. is ~ 1 mg·l^{-1}, then [PuL^{3+}] + [$PuL_2{}^{2+}$] account for ~ 90% of the total [Pu(IV)] in solution. If the concentration of D.O.C. is 0.1 mg·l^{-1} the complexes account for ~ 50% of the total [Pu(IV)] in solution.

The effect of increasing ligand concentrations, presumably D.O.C. on the [Pu(IV)] in solution is also apparent from studies of interstitial water. Nelson and Lovett have shown that the values of ${}^{IV}K_D$ calculated from measured concentrations of Pu(IV) on sediments and in interstitial water taken from the Irish Sea are an order of magnitude lower than the value of K_D in the overlying water.(47) The ratio of [PuV]/[Pu(IV)] decreases from ~ 5.0 in the overlying water to ~ 0.1 in the interstitial water. Presumably the decrease in the value of K_D for Am(III) with increasing sediment/water ratio is also due to a similar complexing reaction.(45) Clayton et al. have shown that concentrations of EDTA greater than 10^{-6} M depress the value of K_D for Am(III) the formation of a complex in solution.(50) However, part of the decrease in the value of K_D may be due to the destruction of the hydrous oxide layer as a result of the complexing of iron etc. It must be stressed that the values of these stability constants are based on the assumption that the stability constants calculated by Allard for the hydroxyl complexes are correct(9), but this has no effect on relative concentrations.

Provided that the formation constants for the hydrolysis of Pu^{4+} are correct, there is no need to invoke complexing by ligands other than OH^- and humic acids. In fact, it can be shown that, even if all the low molecular weight component of D.O.C.in the water is assumed to be present as ligands such as citrate and oxalate - known to form strong complexes with Pu^{4+} ions(11,21) and without considering competitive equilibria with major cations, the complexes formed would not significantly change the concentration of Pu(IV) in solution.

The interplay between the various factors: (1) solubility product, (2) complexing by hydroxyl ions, (3) complexing by humic acid, and (4) the distribution coefficient, is simply illustrated. Each of these factors in their own way limit the total and maximum concentration of plutonium that can remain in solution. This is best illustrated as in Fig. 4 by showing the change in concentration in solution as a function of the total concentration of plutonium in the system (water and sediment).

In the absence of complexing by hydroxyl ions the maximum concentration of Pu(IV) that can exist in solution as Pu^{4+} before a precipitate forms would be 10^{-32} $\underline{M}$. Calculations using the stability constants reported by Allard indicate that complexing by hydroxyl ions increases by a factor of 10^{20}, but the experimental data of Nelson et al.(49) suggests that this factor should be 10^{24} with $[Pu(IV)] \simeq 10^{-8} - 10^{7}$. Complexing of further plutonium by organic carbon will increase this concentration by a further factor of ~ 3.0. This is illustrated in Fig. 4, curves (a) and (b). In the presence of sediment, the total amount of plutonium that can be added to the system before precipitation of $Pu(OH)_4$ occurs will increase by a factor equal to K_D, larger curves (c) and (d). A complication arises when the fraction of adsorption sites occupied by plutonium on the sediment increases beyond ~ 1% and the value of the K_D decreases. In this example it is assumed that the decrease is a factor of 100 between 1% and 100% coverage, a value that appears to be typical for other metals.(38) This is illustrated in curve (d). As the surface coverage is increased the K_D decreases and the concentration in solution moves towards a value limited by a K_D value of 5×10^3 rather than the original $K_D = 5 \times 10^5$.

A further complication will be introduced when the total concentration of complexing ligand $[HL] + [L^-] \approx [PuL_n]$. If the total concentration of plutonium added approaches this value, the concentration in solution will move towards the value governed by just the hydroxyl ion concentration, curves (f) and (e). Finally if exhaustion of ligand occurs before the saturation of surface adsorption sites on the sediment a behavior approximated by the curve (d) - (g) might occur. The behavior of Pu(V) under similar conditions is also show, curve (h).

7. CONCLUSIONS

1. The behavior of the long-lived radionuclides in the oceans is controlled by the formation of complexes and the interaction of specific species with sediments.

2. The maximum concentration of plutonium that can exist in neutral or slightly basic natural waters is influenced by the ratio of [PuV]/[PuIV]. As an univalent ion, the solubility of Pu(V) is large and in equilibrium with PuO_2OH at pH 8, the maximum $[PuO_2^+] \simeq 2.5 \times 10^{-3}$ $\underline{M}$. The maximum [Pu(IV)] at pH 8 approaches 10^{-7} $\underline{M}$, a concentration which is several orders of magnitude higher than would be predicted from published values of K_{So} and hydroxyl ion complexing.

3. Under normal environmental conditions, these radionuclides are under adsorption/desorption control, thus confirming Goldberg's hypothesis of equilibrium distribution,(51) but in situations where extremely large concentrations are discharged precipitation/dissolution could become the major controlling factor.

4. At environmental concentrations of plutonium or americium their effective solubility is controlled by the total concentration of solids present in the system. However, if the total concentrations of Pu or Am added is doubled, the final concentration in solution will be doubled also. Thus expressing solubilities as a percentage of total radionuclide added is meaningless.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the generous support of the U.S. Department of Energy, Office of Health and Environmental Research and the U.S. E.P.A., Office of Exploratory Research during the many years of effort devoted to understanding the behavior of long-lived radionuclides in the environment. They appreciated the fruitful discussions with R.P. Larsen and J. Pentreath during the course of this work.

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STUDIES ON BEHAVIOR OF LONG-LIVED ACTINIDES PLUTONIUM AND AMERICIUM IN THE BALTIC SEA; EFFECT OF SEASON, DISTRIBUTION COEFFICIENTS IN PARTICULATE MATTER AND SURFACE SEDIMENT

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Abstract

Concentrations found are similar to other seas at the same latitude and probably originate from fallout. Both elements increased in concentration in surface waters in summer. Americium was more closely associated with particulate matter than Pu. Analysis of particulates showed similar concentrations to those in surface layers of sediments. K_d values for both were 10^5-10^6, very similar to results reported elsewhere. In contrast to deep sea regions, 2% of Pu and Am were in the water column and 98% in the sediments. A method for separating $Pu^{III,IV}$ and $Pu^{V,VI}$ in water was developed which relies on NdF_3 coprecipitation.

1. INTRODUCTION

The behaviour of transuranic elements plutonium and americium in the water of the Baltic Sea and its Gulfs have been studied since 1979 [1,2]. The first phase of the investigations was to determine the $^{239,240}Pu$ and ^{241}Am concentrations in the water and especially to investigate the distribution of plutonium and americium between filtered seawater and the particulate fraction.

The Baltic Sea and its Gulfs is a shallow brackish water area. The salinity of water samples collected varied between 3 - 8 ‰ in surface waters and 7 - 13 ‰ in bottom waters. The highest sampling depth of our study has been 235 m. In the Baltic Sea there is also a large seasonal variation in temperature. Thus, the conditions in the Baltic Sea are very different from those existing in the locations studied as possible deap-sea dumping sites. This gives an opportunity to consider the effect of some factors on behavior of transuranic elements in marine environment.

During the project period of 1982 - 1984 the effect of seasonal variation and salinity on the distribution of ^{239,240}Pu and ^{241}Am in the Baltic Sea was studied. In addition the distribution coefficients for these radionuclides in particulate matter of water and surface sediments have been calculated.

To understand the interaction of transuranic elements between water phase and particulate fraction (or sediment) information about chemical form and oxidation states are needed. In present study a method for determination the oxidation states of plutonium as a function of sampling depth in the large volume samples was developed.

2. MATERIALS AND METHODS

2.1. Samples

Water and sediment samples have been collected in the Baltic Sea during the years 1979 - 1984. Figure 1 indicates the locations of the sampling stations. Collection of water and particulate samples have been described earlier [1,2].

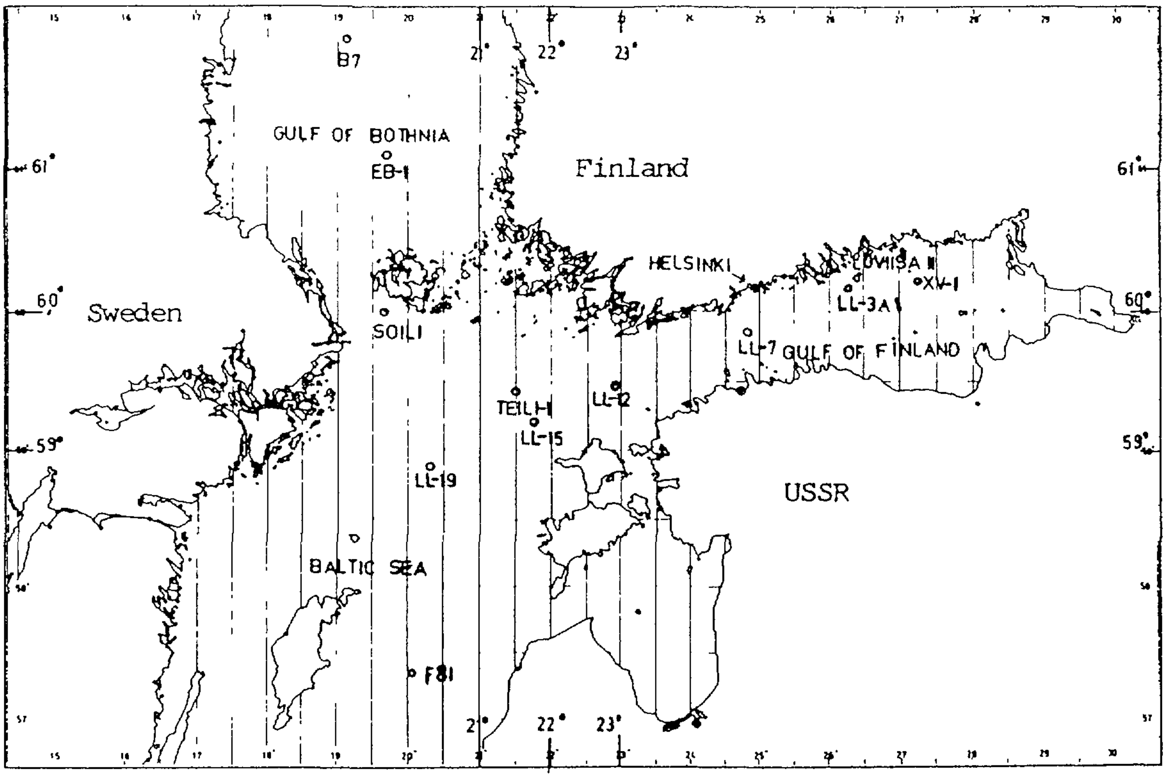


Figure 1. Sampling sites in the Baltic Sea and its gulfs.

The water samples was filtered through Millipore cartridge filter, pore size 0,30 μm. No effect of pore size, in the range of 0.22 - 0.50 μm, on the concentrations and distribution coefficients of Pu and and Am was found. The sediment samples have been taken with a gravity corer having an inner diameter of 21 cm [3] . The cores were split into transverse sections of 1.5 - 5 cm.

2.2. Determination of ^{239,240}Pu and ^{241}Am

The water and air dried particulate samples were analyzed for ^{239,240}Pu and ^{241}Am by procedures reported earlier[1,2]. To improve the chemical yield and separation of ^{241}Am a method reported by Bojanovsky et al [4] and modified at our institute[5] was introduced.

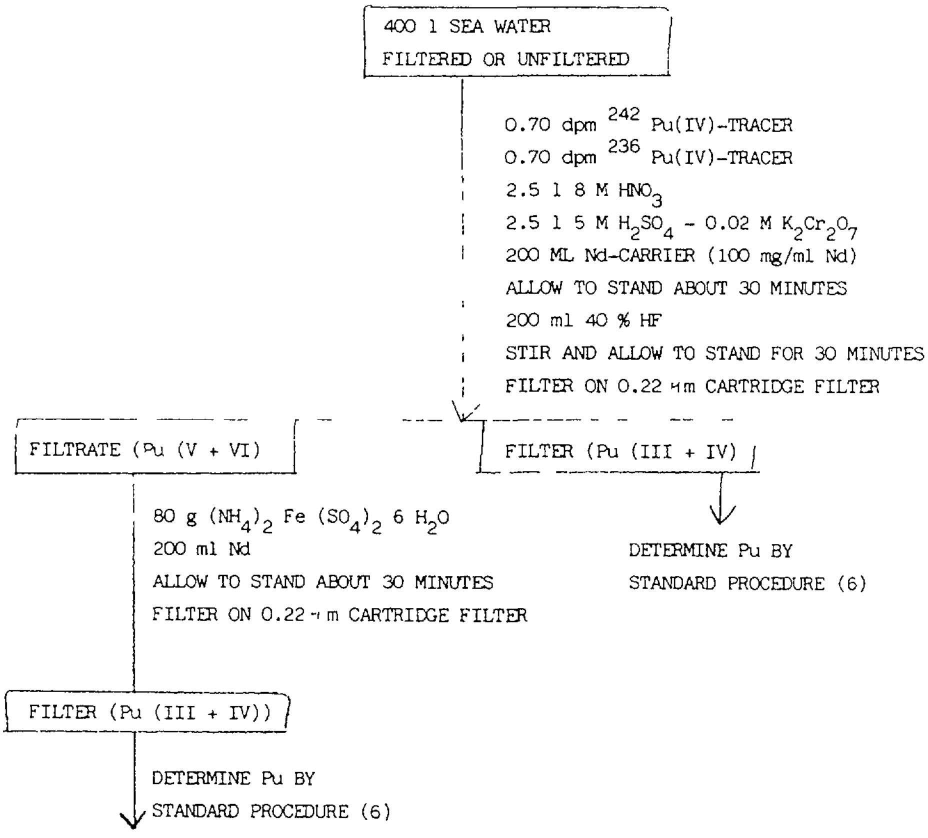
This method is based only on anion- and cation-exchange and it is especially suitable for sediment samples. The alpha-activity of samples were measured with Si-surface barrier semiconductor detector for 3 - 10 days.

2.3. Validity of the results

To check the reliability of the plutonium and americium results the intercalibration samples SW-N-I (seawater) and SD-N-I (sediment) obtained from the IAEA were analyzed.

The reagent background was regularly controlled. The background count rate for alpha-spectrometer used for determination of low ^{239,240}Pu and ^{241}Am concentrations was 0 - 3 and 2 - 5 counts per 10 000 min for ^{239,240}Pu and ^{241}Am energy regions, respectively.

2.4. Separation method for determination of plutonium oxidation states



* IF UNFILTERED IT IS ALLOWED TO STAND 24 HOURS

Figure 2. Determination of the oxidation states of plutonium.

The analytical scheme to separate the lower oxidation states of plutonium (III, IV) from the higher oxidation states (V, VI) is indicated in Figure 2. The method is based on the method suggested by Lovett and Nelson [6]. Pu(IV) will coprecipitate quantitatively on lanthanum fluoride whereas Pu(VI) stays in solution. The holding oxidant, $K_2Cr_2O_7$, was added to prevent reduction of Pu (VI) by any reducing agent and also to oxidize Pu(V) to Pu(VI) as well as Pu(III) to Pu(IV). Both filtered (pore size $0.22 \mu m$) and unfiltered seawater samples were analyzed. Also the particulate matter was analyzed for total Pu.

3. RESULTS AND DISCUSSION

The results for water samples collected in 1981 in the Baltic Sea Proper are given in Table 1. These results will complete our earlier data [1,2].

Table 1. ^{239,240}Pu and ^{241}Am in water of the Gulf of Finland and the Baltic Sea in 1981. The filter pore size used was 0.30 μm. The standard deviation of the radioassay (1 σ) is indicated.

Station	Date of collection 1981	Depth m	Plutonium -239,240		Americium -241	
			Filtered water mBq/m^3	Particles mBq/m^3 (mBq/g dry wt)	Filtered water mBq/m^3	Particles mBq/m^3 (mBq/g dry wt)
LL-7	14.7	surface	6.3 ± 0.7	0.48 ± 0.07	1.5 ± 0.7	0.15 ± 0.07
"	"	60	4.1 ± 1.1	0.26 ± 0.07	1.1 ± 0.4	0.11 ± 0.04
F81	15.7	surface	4.4 ± 0.7	0.18 ± 0.07	-	-
"	"	40	3.0 ± 0.7	0.059 ± 0.022	0.7 ± 0.4	< 0.1
"	"	130	2.2 ± 1.1	0.18 ± 0.07	0.7 ± 0.7	0.18 ± 0.15
"	"	220	4.8 ± 1.1	0.30 ± 0.07	0.4 ± 0.4	0.15 ± 0.07
LL-3A	16.12	surface	6.0 ± 2.2	3.29 ± 0.36 (3.70 ± 0.40)	0.6 ± 0.6	0.60 ± 0.15 (0.67 ± 0.17)
"	"	50	3.4 ± 0.7	1.46 ± 0.18 (1.42 ± 0.17)	0.5 ± 0.5	0.44 ± 0.09 (0.43 ± 0.09
LL-7	17.12	surface	5.0 ± 1.5	1.98 ± 0.46 (2.26 ± 0.53)	0.8 ± 1.0	0.44 ± 0.11 (0.51 ± 0.13)
"	"	50	3.8 ± 1.3	0.97 ± 0.22 (0.73 ± 0.17)	1.1 ± 0.8	0.67 ± 0.16 (0.51 ± 0.12)

The average concentrations of ^{239,240}Pu and ^{241}Am in the Baltic and its Gulfs during 1980 - 1981 were 5.9 ± 2.5 mBq/m^3 and 1.8 ± 0.8 mBq/m^3 respectively. These results are in good agreement with those found in Danish and Swedish waters [7 - 9].

The integrated total concentrations of ^{239,240}Pu and ^{241}Am in the entire water column at the station F81 (depth 235 m) were 0.68 Bq/m^2 and 0.17 Bq/m^2 respectively. Comparing these values with the total cumulative fallout in the water column and sediment core it was found that in 1981 only 2 % of plutonium and americium is present in the water column.

3.1. Vertical distribution of Pu and Am in water column

The variations at different depth are rather small especially for Am. The vertical profile of ^{239,240}Pu content, water temperature and salinity at the deepest sampling site of the Baltic in July is shown in Fig. 3. It can be seen that the vertical distribution of plutonium in filtered water and water particulate has a minimum in water under a sharp thermocline and halocline. The water mass at the depth of the minimum plutonium concentration is surface water originating from previous winter. Similar distribution of plutonium as a function of depth was found in the water columns of the other sampling sites, too.

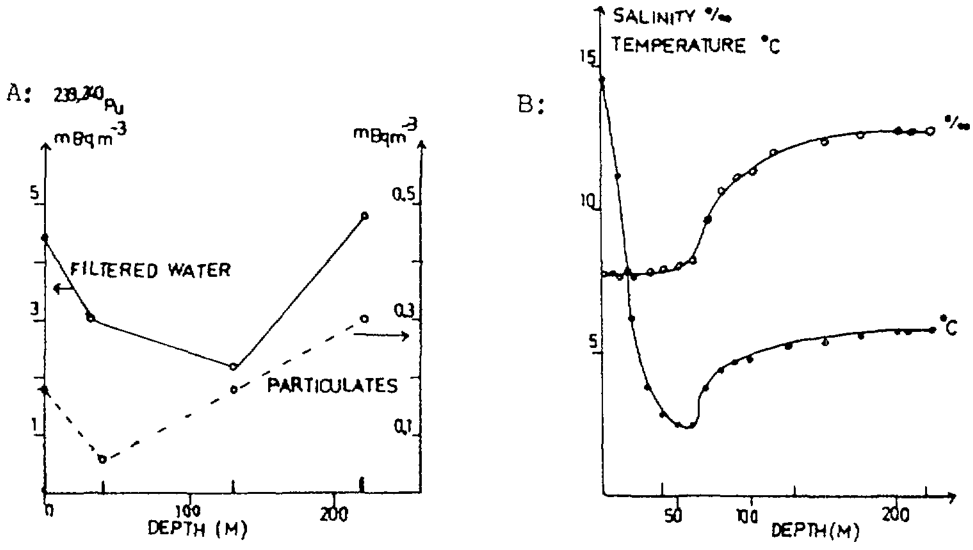


Figure 3. A) ^{239,240}Pu concentration in filtered water and particulate matter as a function of depth.

B) Salinity and water temperature as a function of depth.

The determinations were carried out at the station F81 in July 1981.

3.2. Seasonal variations

No effect of season on total concentrations of ^{239,240}Pu and ^{241}Am in sea water samples of the Baltic Sea was found (Table 1).

The concentrations of ^{239,240}Pu and ^{241}Am in particulate fraction of sea water samples collected at different time of year showed significant differences (Table 1.) [2]. In Fig. 4. the concentrations of ^{239,240}Pu and ^{241}Am in particulate matter of water at the station LL-7 as a function of season are presented. A significant decrease in concentrations of Pu and Am occured in July. These results indicate that plutonium and americium are depleted from the surface water but do not reach bottom water during the summer months. In winter the concentrations of particulate Pu and Am in surface water increased to the concentrations existing in the spring. This is due to the winter mixing period, which can be seen in Fig. 5. In May and July there are a sharp thermocline and halocline at a depth about 50 m. In December the differences of the water temperature and salinity are much smaller because the water bulks are mixed. Similar behavior of Pu and Am as a function of season as at the station LL-7 was found at the other sampling sites, too. The transfer of plutonium and americium to the surface sediment was delayed by the seasonal circulation.

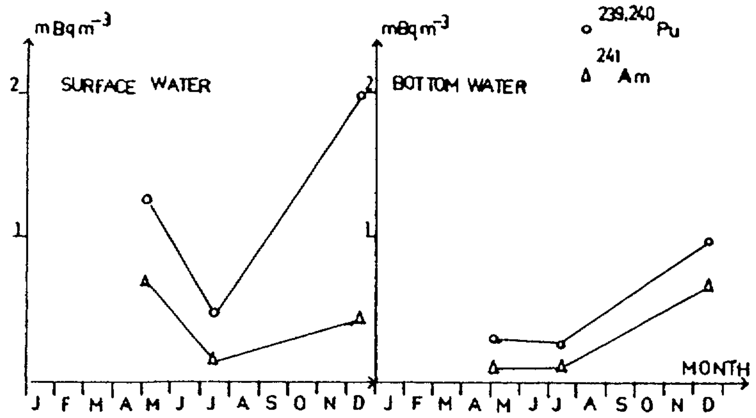


Figure 4. The concentrations of $^{239,240}Pu$ and ^{241}Am in the particulate matter in spring (May 1980), summer (July 1981) and winter (December 1981). Water samples were collected at the station LL-7.

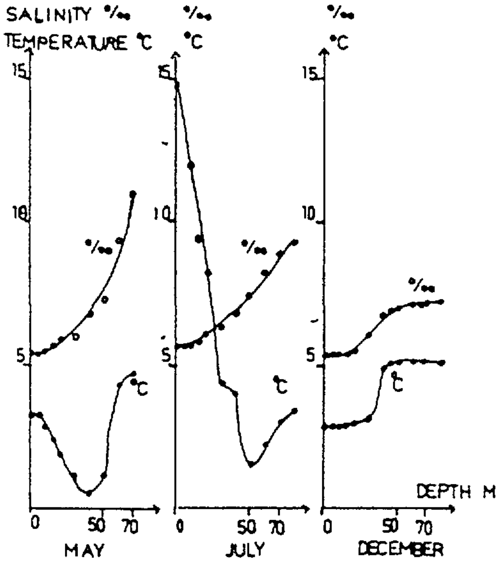


Figure 5. Salinity and water temperature as a function of depth at the station LL-7 in spring (May 1980), summer (July 1981) and winter (December 1981).

3.3 The K_d-values of ^{239,240}Pu and ^{241}Am

3.3.1. Particulates of water

The particulate mass (> 0.30 μm) in water of the Gulf of Finland in December 1981 varied from 0.9 to 1.3 mg/l. Using the concentrations of plutonium and americium in filtered sea water and particulate matter and the total mass of particulates in the water the K_d-factors for ^{239,240}Pu and ^{241}Am were calculated (Table 2.) The K_d-values obtained for ^{239,240}Pu were the same order of magnitude (10^5 ml/g). For ^{241}Am the K_d-values varied from 10^5 to 10^6ml/g. These results are in good agreement with those reported in literature [10, 11].

The higher K_d-values of ^{241}Am compared to those of ^{239,240}Pu agree also with the data presented in Figure 6. The percentages of particulate bounded ^{241}Am are consistently higher than those of ^{239,240}Pu. The average ^{241}Am/^{239,240}Pu activity ratio in particulate matter seems to be higher (0.5 $\pm$ 0.3) than in filtered water (0.3 $\pm$ 0.2). These observations may suggest that americium tends to be more efficiently associated with particulate matter than plutonium.

Table 2. Distribution coefficients (K_d) for ^{239,240}Pu and ^{241}Am in particulates of water (> 0.30 μm) and in surface layer of sediments.

Station	Sample	Date of collection	K_d (ml/g) Pu	Am
LL-3A	Particles, surface water	16.12.1981	6.2×10^5	11×10^5
	" 50 m	"	4.2×10^5	8.6×10^5
LL-7	Particles, surface water	17.12.1981	4.5×10^5	6.4×10^5
	" 50 m	"	1.9×10^5	4.6×10^5
EB-I	Sediment, 0 - 5 cm	04.08.1980	6.0×10^5	2.5×10^5
F81	Sediment, 0 - 1.5 cm	15.07.1981	5.0×10^5	24×10^5
	" 1.5 - 3 cm	"	0.8×10^5	2.3×10^5

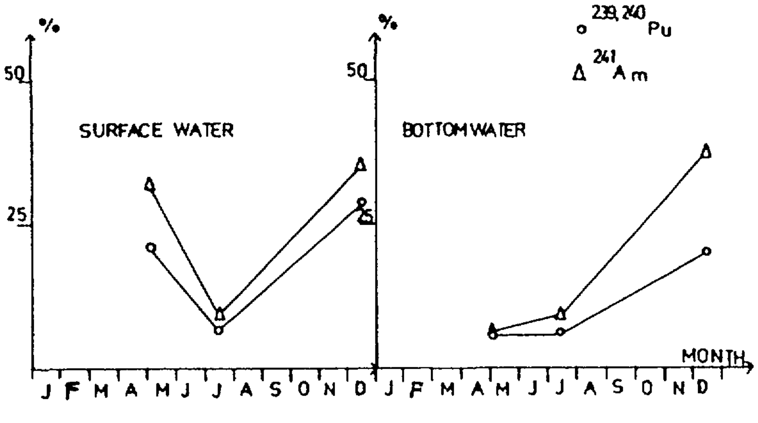


Figure 6. The pergentage of particulate bounded Pu and Am from total concentrations in water. The samples were collected at the station LL-7.

3.3.2. Surface layer of sediments

The total integrated ^{239,240}Pu in sediment cores at the sampling sites of EB-I and F81 were 38 and 26 Bq/m^2, respectively. For ^{241}Am 6.3 Bq/m^2 at the EB-I was obtained. The average activity ratio ^{241}Am to ^{239,240}Pu in these sediment cores was 0.27.

The distribution coefficients of ^{239,240}Pu and ^{241}Am in surface layer of sediments are given in Table 2 . The K_d-values for Pu and Am are the same as in particulates of water being 10^5 ml/g for Pu and from 10^5 to 10^6 ml/g for Am. The K_d-values of Pu and Am for surface bottom sediments (0 - 3 cm) in Danish water are slightly lower, 1.1×10^5 and 3.3×10^5 for Pu and Am, respectively [7] . This is probably due to the higher salinity (30 - 34 ‰) in Danish bottom waters than in bottom water of the Baltic Sea (7 - 13 ‰).

4. SUMMARY

The concentrations of ^{239,240}Pu and ^{241}Am found in the Baltic Sea are very similar to those reported for sea areas located in the same latitude band and where the plutonium present in water predominantly originates from global atmospheric fallout.

A seasonal variation in concentrations of particulate bounded plutonium and americium in surface water was found. There was a significant decrease of Pu and Am concentrations in summer. During the winter mixing period the concentrations increased back to the spring values. Americium seems to be more efficiently associated with particulate matter than plutonium.

The concentrations of $^{239,240}Pu$ and ^{241}Am, expressed as mBq/g dry wt, are the same as those of surface layer sediments. The K_d-factors of $^{239,240}Pu$ and ^{241}Am in particulate matter of water and in surface sediments are the same, too. The average K_d-values for Pu and Am were 10^5 and 10^5 - 10^6 ml/g, resp..These values are in agreement with K_d-values reported for other regions.

In contrast with the deep-sea regions only about 2 % of total integrated concentrations of plutonium and americium in the Baltic Sea was in water and 98 % in sediment [12].

For the determination of oxidation states of plutonium in seawater a method for separation Pu(III,IV) and Pu(V,VI) from large volume water samples was developed. This method is based on the NdF_3-coprecipitation. The oxidation states of plutonium will be studied especially at deep sampling sites (e.g. Gotland deep, F 81) where the hydro-chemical observations indicate practically oxygen-free conditions and high H_2S-concentrations in bottom water.

ACKNOWLEDGEMENT

This investigation was financially supported by the Finnish Ministry of Trade and Industry.

We gratefully acknowledge the collaboration with the Institute of Marine Research, Helsinki.

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MARINE BEHAVIOUR OF LONG-LIVED RADIONUCLIDES (FALL-OUT) AT THE PROPOSED DISPOSAL SITE OF RADIOACTIVE WASTES IN WESTERN NORTH PACIFIC*

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Abstract

Water and marine sediment was sampled Analysis was for ^{90}Sr, ^{137}Cs, ^{60}60, ^{239,240}Pu, and ^{230,232}Th. The integrated values of ^{90}Sr and ^{137}Cs were 78 and 120 mCi km^{-2}, similar to GEOSECS figures. All isotopes were detected in sediment, which indicates fast sinking particulate material transport, since water depth is 6000m. Cores showed bioturbation effects surprisingly often. Pu penetrates to about 15 cm, ^{137}Cs to 20cm Inventory values for 1980-1983 for water and sediments gave the following ranges; ^{90}Sr (water) 78-89 mCi km^{-2}, (sediment) 0.03-0.09; ^{137}Cs 115-151 and 0.53-0.91 respectively; ^{239}Pu (sediment) 0.09-0.12. These are smaller than for the Atlantic.

1. Introduction

In Japan, land disposal and deep sea disposalhave been discussed as the disposal methods of solidified low level radioactive waste.

As for the latter, a proposed disposal area was chosen in the western north Pacific, and now we are conducting environmental research such as bottom topography, geology, deep current, diffusion, marine organisms and radioactivities of marine environments. Among them,the measurements of radioactivity of sea water and seabed sediments have been carried out by the Hydrographic Department of Maritime Safety Agency at the proposed disposal site.

At this site, the solidified low level radioactive wastes have not yet been disposed, therefore, all radioactive materials which we are measuring are global fallout radionuclides derived from the atomic bomb tests.

Research about the radioactivity level and the behavior of fall out radioactive nuclides at this area are very important to assess the effects of ocean disposal of solidified low level radioactive wastes on the marine environment in the western north Pacific in advance of disposal operations.

In this report, the results of radiological researches conducted from 1980 through 1983 by the Hydrographic Department at the proposed disposal site for test disposal of solidified low level radioactive wastes are described.

2. Research area

The research area (named as B area) is 900 km south east of Tokyo and 100 km square centered at 30 N, 147 E (Fig.1). The bottom in this area is mostly flat and covered with soft red clay (1). Manganese nodules have been scarcely found. The mean depth is approximately 6200 m.

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[*] Part of IAEA-coordinated research programme on the "Marine Behaviour of Long-Lived Radionuclides Associated with the Deep-Ocean Disposal of Radioactive Wastes".

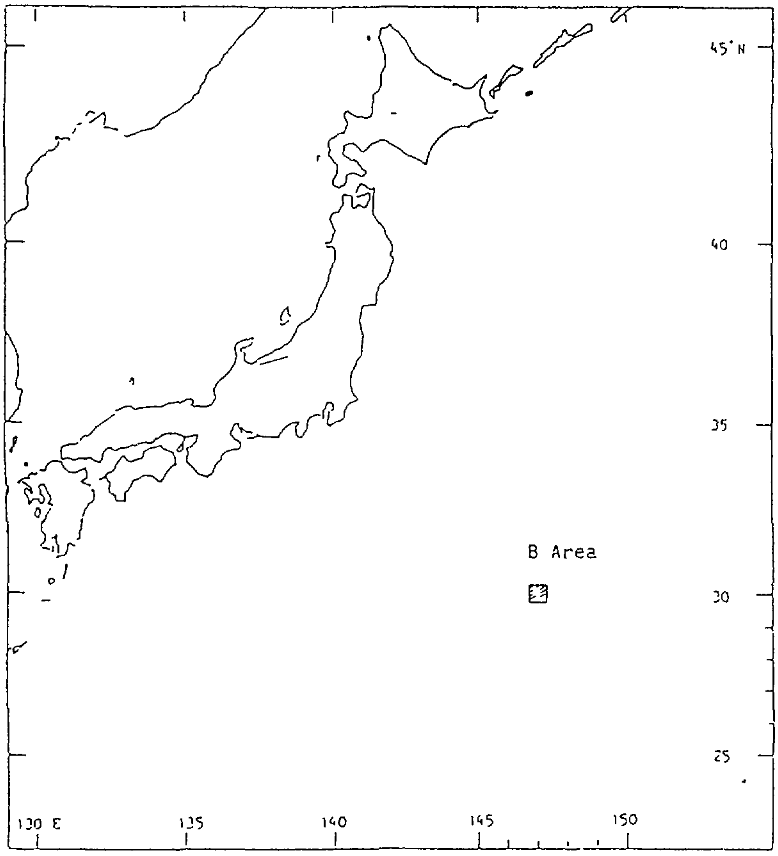

Fig. 1. Proposed ocean disposal site for radioactive solid wastes

3. Sampling and pretreatments

Sampling of sea water and marine sediments for the radiochemical analysis were carried out on board the Hydrographic Department surveying ship "Syoyo" (1842 tons). Sampling locations were determined by a combination of rolan C and NNSS. Sampling locations of sea water and marine sediments are shown in Fig. 2. Sea water samples were collected at several stations in each year. At one station among them, sea water samples were collected from about 12 layers from a 10 m layer to near a bottom layer. At other stations, only two water samples were collected from 10 m and 100 m above the bottom respectively. The sampler used is made of polypropyrene and 100 liters volume. The distance of the sampling layer from the bottom was determined by a pinger at the bottom water sampling. Sea water samples were acidified by adding hydrochloric acid immediately after the sampling and brought to Tokyo where the radiochemical analyses were performed.

Marine sediment samples were collected at several stations in every year by using a Smith-McIntyre grab sampler. Sediments from top to 2 cm depth were taken. At some stations among them, three more sediment samples deeper than 2 cm were taken. These deeper slices were 3 cm thick. 2-5 cm, 5-8 cm, 8-11 cm.

At the center of the proposed area, a core sediment sample of about 85 cm length was taken by using a gravity corer with a 9 cm diameter. The sample was divided on board into 17 segments of 5 cm thickness except for the top one which was 2.5 cm thick.

4. Radiochemical analysis

Radionuclides analysed were Sr-90, Cs-137 and Co-60. They were selected taking into account the contents of low level radioactive wastes which are to be disposed and the half lives of the radionuclides.

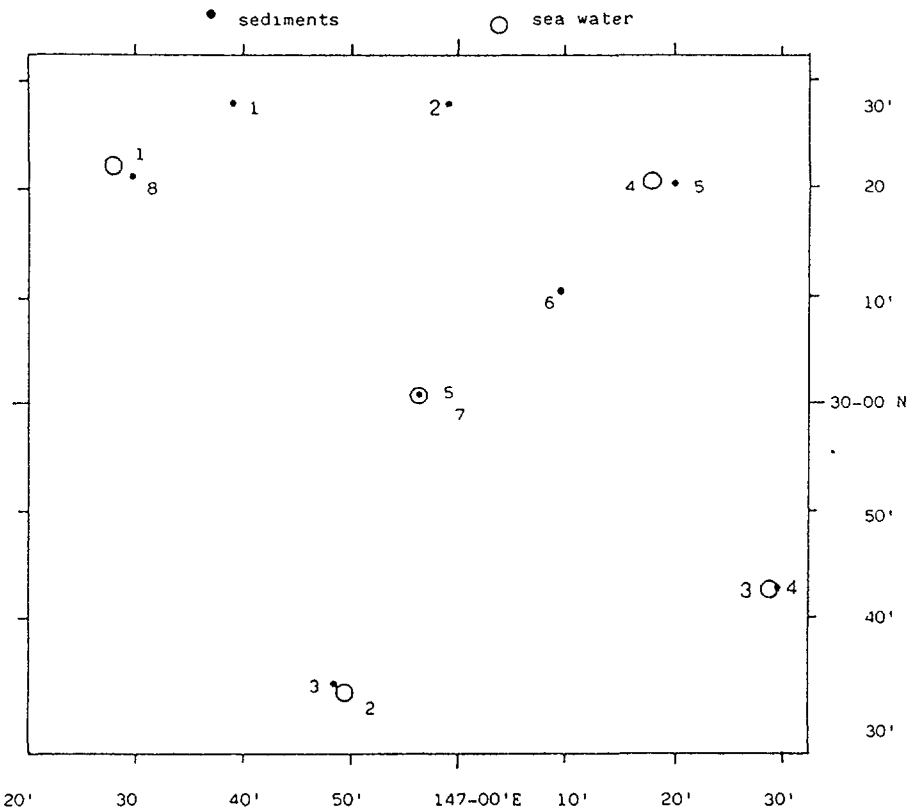

Fig.2. Sampling locations of sea water and marine sediments

Although the plutonium content of low level radioactive wastes is very small, the half life of plutonium-239 is very long (2.44×10^4 years). Plutonium analysis was also made on the marine sediment sample.

Core sediment samples collected at St. 1 by gravity corer were analysed for Th-230,232 in addition to Pu-239,240, to discuss the possibility of bioturvation effects.

Outlines of analytical procedures are as follows.

4.1 Sea water

4.1.1 Cs-137

Sea water sample was acidified by adding hydrochloric acid and cesium was adsorbed to ammonium phosphomolybdate and precipitated. After the precipitate was dissolved in alkali media, cesium was separated from rubidium by cation exchange column chromatography with Duolite C-3 resin. The radioactivity of cesium-137 was measured by low-background gas-flow counter as cesium chloroplatinate which had been previously filtered on filter paper, was dried and weighed.

4.1.2 Sr-90

Strontium was precipitated as carbonate with calcium from the water sample in which cesium-137 was previously separated off. The carbonate precipitate was dissolved in acid and left for a period of more than 2 weeks after addition of yttrium carrier. Yttrium was precipitated as hydroxide with magnesium hydroxide precipitates and was purified by cation exchange column chromatography (2) and solvent extraction method using HDEHP (3). The radioactivity of Y-90 was measured by low background gas flowcounter as yttrium oxalate which was previously filtered on filter paper, dried and weighed.

4.1.3 Co-60

Cobalt which was precipitated together with carbonate precipitates of calcium and strontium was separated from alkaline-earth metals as hydroxide precipitates and then purified by anion exchange column chromatography with hydrochloric acid and then cation exchange column chromatography with tetrahydrofuran (THF)-hydrochloric acid mixture (4). Cobalt was at last electroplated on copper plate. The radioactivity of Co-60 was measured by low back ground beta-ray spectrometer.

4.2 Marine sediments

4.2.1 Co-60

Cobalt was leached from sediment sample by hot 8N hydrochloric acid and separated from large amounts of iron, aluminium and manganese by anion exchange column chromatography by Kraus method and cation exchange column chromatography by using the tetrahydrofuran (THF)-hydrochloric acid mixture as eluent. The purified cobalt was electroplated on copper plate. The radioactivity of radiocobalt was measured by low back ground beta ray spectrometer.

4.2.2 Cs-137

The effluent of the anion-exchange column operation of cobalt analyses was used for cesium and strontium analysis. Cesium was adsorbed on ammonium phosphomolybdate precipitate and precipitated and thereafter procedures were the same as procedures of sea water analysis.

4.2.3 Sr-90

The solution from which ammonium phosphomolybdate precipitates were filtered was used for the determination of strontium-90. Strontium was concentrated by precipitation as carbonate and then treated by the same procedures as sea water analysis.

4.2.4 Pu-239,240

Known amount of Pu-242 (for the samples collected in 1982, Pu-236) which was calibrated by NBS was added to the marine sediment sample and then leached by hot 8N nitric acid. After the Pu was oxidized, the leached solution was passed through an anion exchange column. Pu was purified by washing the column with nitric acid and then hydrochloric acid. Pu was eluted by hydrochloric acid containing ammonium iodide. Purified Pu was electroplated on stainless steel plate. The radioactivity was measured by alpha ray spectrometer.

4.2.5 Th-230,232

Thorium was leached by acid solution from the sediment sample and purified by anion exchange column chromatography in nitric acid medium. Purified thorium was electroplated on stainless steel plate and radioactivity was measured by alpha ray spectrometer.

5. Results and discussion

5.1 Sea water

The vertical distributions of Sr-90 and Cs-137 from near surface to 10 m above the bottom are shown in Fig. 3 together with those of water temperature and salinity. Sr-90 and Cs-137 are almost identical throughout the surface layer (0-500 m) and the concentrations of these nuclides decrease abruptly from 500 m with depth. At deeper than 1500 m, we could hardly detect these radionuclides by using 100 liter sea water samples.

These features of vertical distribution have been almost the same since 1980 when the vertical observations were begun. The only exception is the decrease of radioactivities of these nuclides in the surface layer.

The integrated values of Sr-90 and Cs-137 are 78 and 120 mCi/km^2 respectively and they are slightly decreasing. These values are fairly equal to the values obtained during GEOSECS observations (5) and the values in the North Atlantic (6) taking into consideration of latitudinal variation of inventory.

5.2 Marine sediments

The concentrations of Pu-239,240, Cs-137, Sr-90 and Co-60 in the uppermost 2 cm layer are 1.6-4.2, 7.1-32.6, 0-3.9 and 0.1-2.5 pCi/kg-dry respectively.

There is remarkable difference between the results of the radioactivities of sea water and those of sediments: Cs-137 and Co-60 are concentrated in sediments compared with Sr-90. Co-60 was detected in sediments which has not been detected in sea water samples. The detection of these artificial radionuclides in deep sea bottom over 6000 m depth may indicate the presence of particulate materials which concentrate some artificial radionuclides considerably and sink fast to sea bottom.

As for the temporal variations of these nuclides, any variation was not observed since 1977 except the gradual decrease of Co-60 by its short half life.

The vertical distributions of Pu-239,240 and Cs-137 in marine sediments since 1981 are shown in Fig. 4. These vertical distributions are classified into two types. The first types are those concentrations of radionuclides which decrease with depth, the second type are those concentrations of radio-

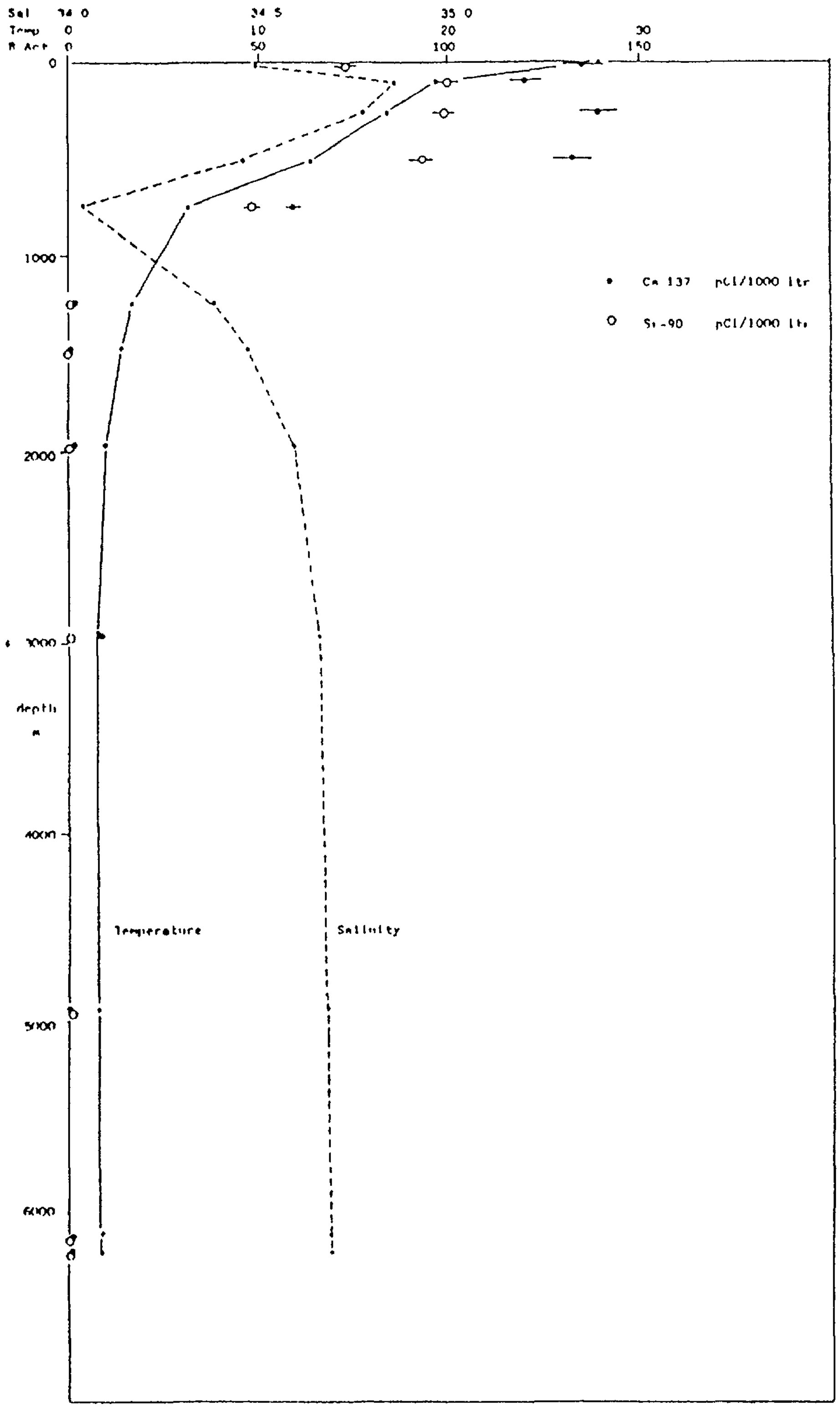

Fig. 3 Vertical distributions of ^{90}Sr, ^{137}Cs, temperature and salinity

nuclides which do not decrease conspicuously with depth. The former distribution indicate that the sediments are not so disturbed by biomaterials in sediments while the latter indicates that the sediments are considerablly disturbed by bioturbation.

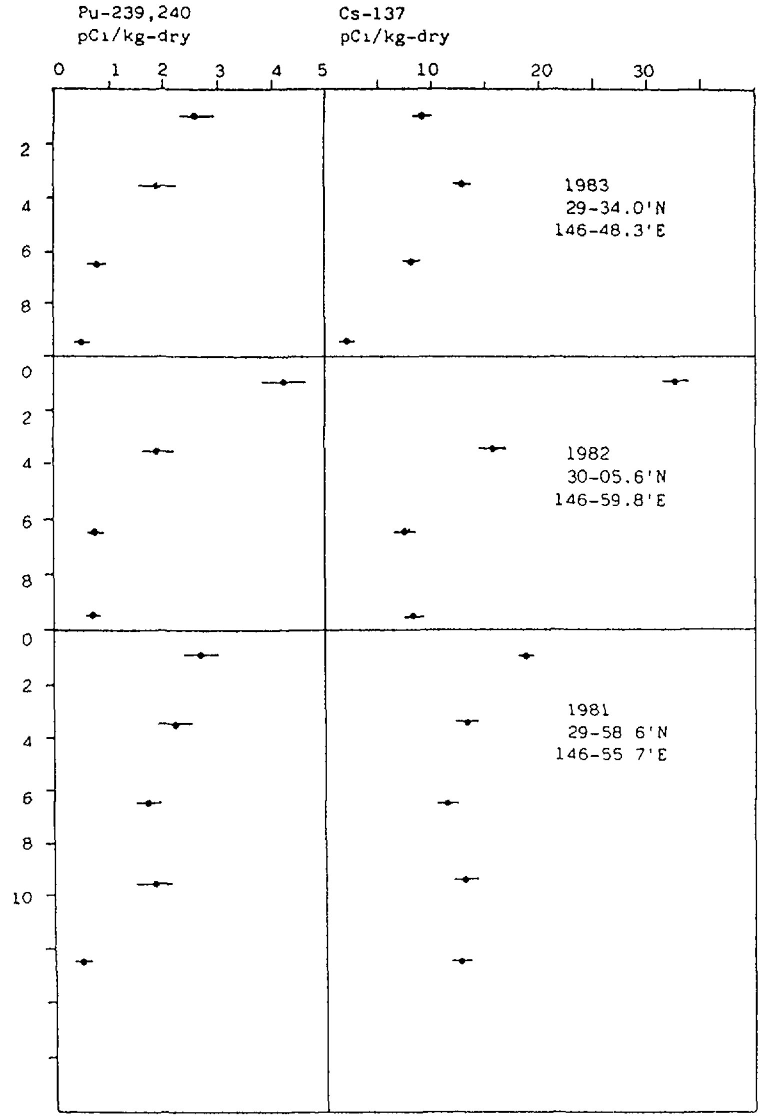

Fig. 4. Vertical distributions of Pu-239 and Cs-137 in sediments

To determine whether this bioturbation reaches a depth of more than 10 cm or not, a 90 cm depth core sample was taken by using a 9 cm diameter gravity corer. Ionium and Th-232 were also analysed, as well as Pu-239,240 and Cs-137. The results are shown in Fig. 5 and 6. As apparent from these figures, Pu-239,240 penetrate to about 15 cm depth. Though it was difficult to say clearly owing to the large counting error, Cs-137 reached about 20 cm depth. The vertical distribution of the ratio of Th-230/Th-232 indicated exponential decrease down to 40 cm depth which corresponds to an age of 10.6 x 10^4 years. Mean sedimentation rate is calculated as 3.75 mm/10^3 y. Below the 40 cm depth, ratios are disturbed down to 65 cm depth. As this disturbance is observed at other part of the ocean (7), it may be due to other causes than bioturbation. Below 65 cm, ratios exponentially decrease again. These results considerably agree with other investigator's results (7).

In the present core, the remarkable effects of bioturbation are not observed in the vertical distribution ratio of Th isotopes in the sediment column from surface layer through 40 cm depth. The concentrations of Pu-239,240 and Cs-137 also decrease abruptly with depth.

In Fig. 6, two more vertical distributions are shown, which illustrate ratios that suffered the effects of considerable bioturbations.

On the other hand, in the sediment samples collected by Smith McIntire grab sampler, we found 1 cm diameter and several cm long green burrowing worm.

In conclusion, in some part of this area, marine sediments are not so disturbed by biomaterials, but in other part, they are considerably disturbed.

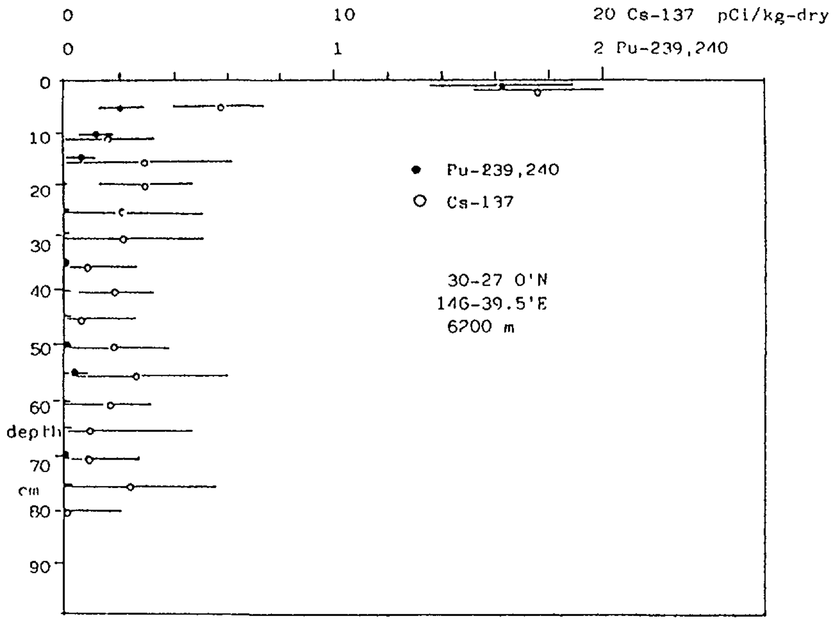

Fig. 5. Vertical distributions of Pu-239 and Cs-137 in core sample

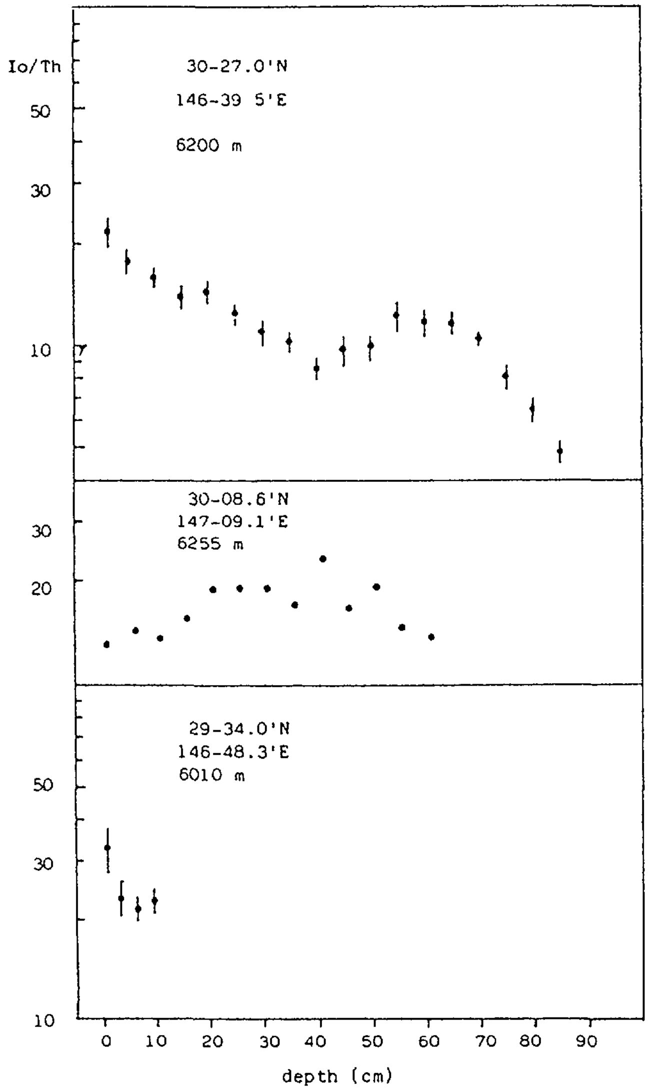

Fig. 6. Vertical distributions of Th-230/Th-232 in core sample

Integrated radioactivity from surface to core bottom was calculated and the results are shown in Table 1. Temporal and horizontal variation of the integrated values was not observed but these values are relatively smaller than those in deep sea sediments of the Atlantic Ocean. These difference may be due to the latitudinal variations of plutonium inventory in the Pacific Ocean.

Table 1. Inventory values of ^{90}Sr, ^{137}Cs, $^{239,240}Pu$ in sea water and sediments (mCi/km^2)

		1980	1981	1982	1983
Sea water	Sr-90	89		82	78
	Cs-137	151		115	120
Marine sediments	Sr-90		0.07	0.09	0.03
	Cs-137		0.91	0.77	0.53
	Pu-239		0.12	0.09	0.09

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NORDOSTATLANTISCHES MONITORING PROGRAMM (NOAMP)

An environmental study of the deep layers of the North-East Atlantic[*]

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Abstract

The NOAMP area is 46°-48°30' N 18°-22°W. Topographic details are given and distribution of sediments, with comments on sedimentation and geology. Eight vertical profiles for ^{137}Cs were taken down to depths of about 5000 m. Down to about 500 m the layer is well mixed and concentrations vary between 2.52 and 5.56 mBq l^{-1}. Within 100-200 m of the bottom a slight increase of ^{137}Cs is observed, which is assumed to be due to the nepheloid layer. The hydrography is variable and described in detail. Bottom current measurement results are described and results of a model for dispersion based on the above findings.

1. Introduction

The NOAMP area extends from 46° to 48° 30' North and 18° to 22° West (Fig. 1).

The field work of NOAMP covers the period from 1983 to 1985.

During spring and fall there is a NOAMP-cruise with the research vessel METEOR to study the regional

- bathymetry and geology
- radiochemistry and marine chemistry
- water masses and nepheloid layers
- water transports, especially within the near-bottom layer.

Additionally, the research vessels POLARSTERN and SONNE undertook bathymetrical, geophysical and geological surveys in the framework of NOAMP.

The primary aim of these investigations is the description of the regional water transports at great depths. Of special importance are dispersion and the pathways of suspended matter within the near-bottom layer as well as the possible transports from the sea floor upwards into the interior of the ocean.

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[*] Supported by the Bundesminister für Forschung und Technologie and performed by the Deutsches Hydrographisches Institut, Hamburg.

Besides the observational work theoretical studies are going on within the framework of NOAMP. Models simulating the circulation and dispersion in the North Atlantic are used to complement and to improve the final conclusions provided by the field measurements.

The following brief descriptions are intended to give an impression of preliminary observational results from the first cruise (NOAMP I) during Sept./Oct. 1983 as well as some examples of the current modelling effort.

2. Geology and Bathymetry

For NOAMP the following geological issues are of interest:

- the topographical features of the ocean floor,
- the compositions of the sea bed materials and their regional distribution,
- the thickness and the spatial structure of the sedimentary cover lying upon the basaltic ocean crust,
- the processes of sedimentation and redeposition of particulate matter.

The results presented here are qualitative observations rather than quantitative results, except the seismic and topographic mapping performed with the SEA BEAM Systems of R/V POLARSTERN and RV SONNE.

A literature review of the surrounding area is given by R. B. KIDD (1983).

Topographic mapping during two cruises in 1983 (central NOAMP box, N 47° - 47° 30', W 19° 30' - 21°) and in 1984 (easterly extension, N 47° - 48°, W 18° 40' - 19° 30') yielded a high quality map of the ocean floor. The depths range between 3600 m and 4600 m. Maximum slope angles are about 15°. The main feature is a system of valleys extending in a North-South direction which are separated by chains of hills and ridges. Seismic reflection records with the Pneuflex-Airgun revealed basaltic basement ridges as the internal cores of the hill chains, which strike parallel to the Mid-Atlantic Ridge (MAR). The sediment cover of these ridges is rather thin, whereas the valleys contain a sediment filling of up to several hundreds of meters (Fig. 2).

The microphysiography of parts of the sea floor proved to be unfavourable for structural investigations of the uppermost sediment with an acoustic sub-bottom profiling system (3.5 kHz - SBP) due to the physical properties of the system employed. A noisy and hyperbolic reflection record resulted apparently due to rough surfaces of the hills. Areas with a thicker sediment cover reveal a set of distinct reflectors parallel to the sediment surface, but of unknown origin. For their identification and for stratigraphic purposes long piston cores were taken (11.5 m recovery).

Box grab samples were taken from the crest of a hill (height: 700 m) along a transect extending 4 nautical miles away from the hill foot. The surface sediment is a tough and sandy lime mud produced by coccolith shields and foraminiferal tests (mainly G. inflata). On the hill and at the site furthest from it one observes buried and uncovered glacial marine remains of continental origin. The region immediately at the foot of the hill is free of these clastites.

There are also differences in the uppermost 50 cm as can be seen from the box grabs: On the hill crest and at the deep plain positions the lime mud is underlain by a tough clayey marl, rich in glacial sand and gravel. The transition between these two layers is relatively sharp, but there is a continuous increase of clay content in the samples from the hill foot without any coarse glacial remains (Fig. 3). The sediment is pasty and exhibits intense bioturbation phenomena.

A 5 m long piston core from the deep plain showed at its base sharp glassy volcanoclastites mixed with angular quartz, plagioclase and sandstone remains, as well as shell relicts of shallow water mollusks.

Depending on the topographic features, the NOAMP area is part of the abyssal hill region. The relief is formed by ridges of oceanic basement rocks which strike parallel to the MAR. The ridges have a thin sediment cover whereas the sediment thickness in the valleys is considerably larger. The recovered surface sediments consist of calcareous mud above a clayey marl, both with various amounts of glacial marine remains. At first sight two sedimentary processes seem to be of great importance: the primary supply of pelagic and glacial marine material through the water column from the sea surface down to the ocean floor, and a subsequent transport of very fine grains from the hill crests down to their immediate foot regions.

9.3. Radiochemistry (^{137}Cs)

Within the framework of NOAMP (North East Atlantic Monitoring Programme) eight vertical profiles of the ^{137}Cs activity concentration were obtained. The positions and depths of these eight stations are given below in table 1.

Station 1	41°	03,3' N	13°	04,0' W	5270 m	
Station 2	42°	14,8' N	14°	15,4' W	5240 m	previous dumpsite
Station 3	42°	30,2' N	14°	29,6' W	5255 m	
Station 4	46°	02,7' N	16°	13,7' W	4175 m	actual dumpsite
Station 5	45°	59,0' N	17°	15,7' W	4710 m	
Station 31	47°	25,8' N	20°	55,0' W	4470 m	NOAMP area
Station 54	47°	18,5' N	20°	06,0' W	4490 m	
Station 59	47°	21,6' N	19°	35,5' W	4420 m	

Table 1: Positions and water depths of the eight radiochemical stations on METEOR-cruise 65 in Sept./Oct. 1983

Samples at up to 16 different depths were taken at each station. Due to the decreasing concentration of artificial radionuclides with depth (Kautsky et al., 1977, Feldt et al., 1981), the sample volume had to increase with depth: from 50 l at the surface to 400 l below 2000 m and 500 l close to the bottom below 4000 m.

The ^{137}Cs activity concentrations of the NEA dumpsites and reference locations are shown in Figs. 4 and 5, respectively. A well-mixed surface layer was found down to 500 m depth with some peak values.

The values of this layer vary between 2,52 (±0,17) and 5,56 (±0,23) mBq/l. From 500 m depth to about 4000 m the values decrease by 50 % approximately every 550 m. Some values are below detection limits (about 0,1 mBq/l). Within 100 to 200 m above the bottom, a slight increase of ^{137}Cs concentration is observed. As the water was not filtered, it is conceivable, that this slight increase is due to the particle concentration of the nepheloid layer. It is not the result of locally dumped radioactive waste, because in the NOAMP area (where no dumping takes place) similar trends are found.

There is no significant difference between the profiles obtained at the dumpsites (Fig. 4) and those obtained at the reference locations (Fig. 5). The values are consistent with fallout levels.

9.4. Hydrography

During NOAMP I a grid of 80 stations were surveyed by means of a Neil-Brown-CTD-System including a nephelometer together with a rosette sampler. The CTD work was cooperative between DHI, Hamburg, and PROSPER, Neuchâtel. The spacing of the grid was 10 n.mi. and 20 n.mi. respectively (Fig. 6).

The CTD-casts all reached to within 5 - 20 m of the sea floor. Water samples were taken to calibrate salinity and to determine oxygen content, phosphate and silica at 13 depths.

All parameters show a distinct variability throughout the whole water column, suggesting that in the NOAMP box different water masses exist side by side down to great depths. The θ-S diagrams show large differences in the surface layer down to about 125 m, uniformity in the θ-S domain of the North-East Atlantic Central water below the surface layer, and again large variations around the core of the Mediterranean Water between 650 m and 1250 m (Fig. 7). The salinity minimum of the Middle North Atlantic Deep Water (MDW) originating in the Labrador Sea (Lee and Ellett, 1965) is clearly visible at most of the stations below the Mediterranean Water.

Whether the observed relative salinity maximum below the MDW is due to eastern Overflow Water coming from the North or whether it is caused by Mediterranean water, which has been mixed down to about 2000 m far away from the NOAMP area and is then laterally transported to the NOAMP site is uncertain. The water below 3000 m fits well in the characteristic θ-S relationship found to be valid at many sites in the North-East Atlantic (Saunders, priv. comm.).

The profiles of oxygen and phosphate show considerable scatter as well (Figs. 8 and 9). Maximum variations are within the layer of the Mediterranean water around 1000 m depth and in the layer of the relative salinity maximum in about 2500 m. Also in the layer close to the bottom the differences of oxygen and phosphate between the stations clearly exceed the accuracy of the determination.

5. Near-Bottom Currents

About 7 long-term moorings with 40 to 50 current metres are in operation for the period from fall 1983 until fall 1985. They are to be replaced every half-year. Five moorings with 5 to 6 current metres each cover the 300 m thick layer above the deep sea bottom (water depths between 3600 and 4800 m). Two moorings cover the water column up to 400 m below the sea surface (12 current metres each). The two lowest instruments at 10 and 30 m above the bottom are acoustic vector averaging current metres (Neil Brown). The other current metres are Aanderaa (RCM5).

Additionally use is made of 3 moorings of the Centre Océanologique de Bretagne, Brest, which have been deployed in the framework of 'Topogulf'. These moorings within or near the NOAMP-area, respectively, have been out deployed for one year and have been replaced by a single one-year mooring during summer 1984. All French moorings have been and are equipped with a NOAMP current metre close above the bottom.

Moreover a joint field project will be carried out between the Centre Océanologique de Bretagne and the Deutsches Hydrographisches Institut, Hamburg, using deep sea neutrally buoyant floats in the NOAMP-area. The float experiment is scheduled for one year starting in spring 1985 with METEOR. The 14 floats are supposed to move at a prescribed depth of 3500 m. There will be 4 listening stations moored in the NOAMP-area.

During some cruises short-term current measurements with a higher sampling interval of 5 to 10 minutes during periods of 1 to 3 weeks are carried out by means of deployed current metres.

One example is short current measurements of about 17 days duration during NOAMP I by means of deployed current metres. Fig. 10 represents the vector velocities averaged over the whole observation period at 5 positions. The topography displayed in Fig. 10 is the result of an echo sounder survey of R.V. POLARSTERN in May 1983 of the central NOAMP-box.

The moorings are 10 to 20 n.mi. apart. The current records reveal remarkable differences of the mean flow within the near-bottom layer at the various mooring positions (Figs. 10 and 11). This apparently has to do with the roughness of the local topography. Among points of special interest is the obvious large deviation of the mean flow direction 10 m above the bottom relative to the flow direction at 30, 70, 150, 200, and 250 m height above the sea floor (Stat. K1, K2, K5).

The mean speeds within the layer close to the bottom range between 1 and 6 cm s^{-1}. The most important short-term current variations (not shown here) are caused by the semi-diurnal tidal currents. The semi-diurnal speeds are about 5 cm s^{-1}. Occasionally topographically induced inertia currents seem to occur. The maximum speed of the overall current reaches about 14 cm s^{-1}.

9.6. Modelling

The field work of NOAMP is supplemented by numerical simulations on the transport by an annual mean flow and mixing of radionuclides in the North Atlantic Ocean. The underlying current field is computed using a model developed by Bryan (1969) and Semtner (1974). The results of this calculations are to some extent questionable especially at great depth. (For a detailed discussion see Bork, Schulte, Mittelstaedt, 1983.) The model itself is, at present, the standard model for three-dimensional circulation calculations of the ocean and therefore the best and most reliable model, which can be handled with a reasonable effort.

The reason for including the transport by the mean circulation in a dispersion model, at all, is that the distribution of activity concentration due to a radioactive source in the ocean is assumed to be primarily determined by advection and only secondarily by mixing. That is, the resulting distribution will be inhomogenous in space, even if a temporarily steady state will be reached.

The present application of the model covers the Atlantic from 30° S to 70° N. It has a horizontal resolution of one degree and 17 layers of different thickness.

From the three-dimensional mean annual current field of the model, particle paths have been derived. As an example a particle source is assumed in the NOAMP area at a depth of 4700 m (Fig. 12).

The released particle moves slowly northward at depth during the first 30 years. After 90 years it emerges near the continental slope at a depth of about 1000 m and continues its way until it approaches the continental slope off Morocco at depths of about 1400 m after 100 years.

For comparison the trajectory of a particle starting at 3200 m depth is described in Fig. 13. The particle remains in the NOAMP area for about 10 years. After the first decade it ascends and moves, in general, towards the South and later towards the West. During a period of about 65 years it crosses the North Atlantic and turns with the Gulf stream back eastward. The return transport from the east coast of the United States to the region between Iceland and Europe takes less than about 15 years.

Other series of numerical experiments deal with Eulerian calculations simulating a continuous radioactivity source of 1000 TBq per year in the NOAMP area at a depth of 4500 m (TBq = Tera Bq = 10^{12} Bq).

Examples of these experiments are shown in Figs. 14 and 15. The figures represent model results on the concentration of activity at 3000 m and 500 m depth, 100 years after the first release. For these simulations a half life of 30 years and diffusion coefficients $A_H = 10^7$ cm^2 s^{-1} and $A_V = 1$ cm^2 s^{-1} are assumed.

Figure 16 indicates the temporal adjustment of the maximum activity concentration at various depths. The diagram suggests an equilibrium of the concentration throughout the water column after about 100 years. At the source depth (4500 m) the equilibrium sets in already after about 10 to 20 years of a continuous release of radionuclides with a half life of 30 years.

A vertical profile of the maximum equilibrium activity concentration composed of the maximum concentration at each model depth is shown in Fig. 17. The maximum indicates the source depth of 4500 m.

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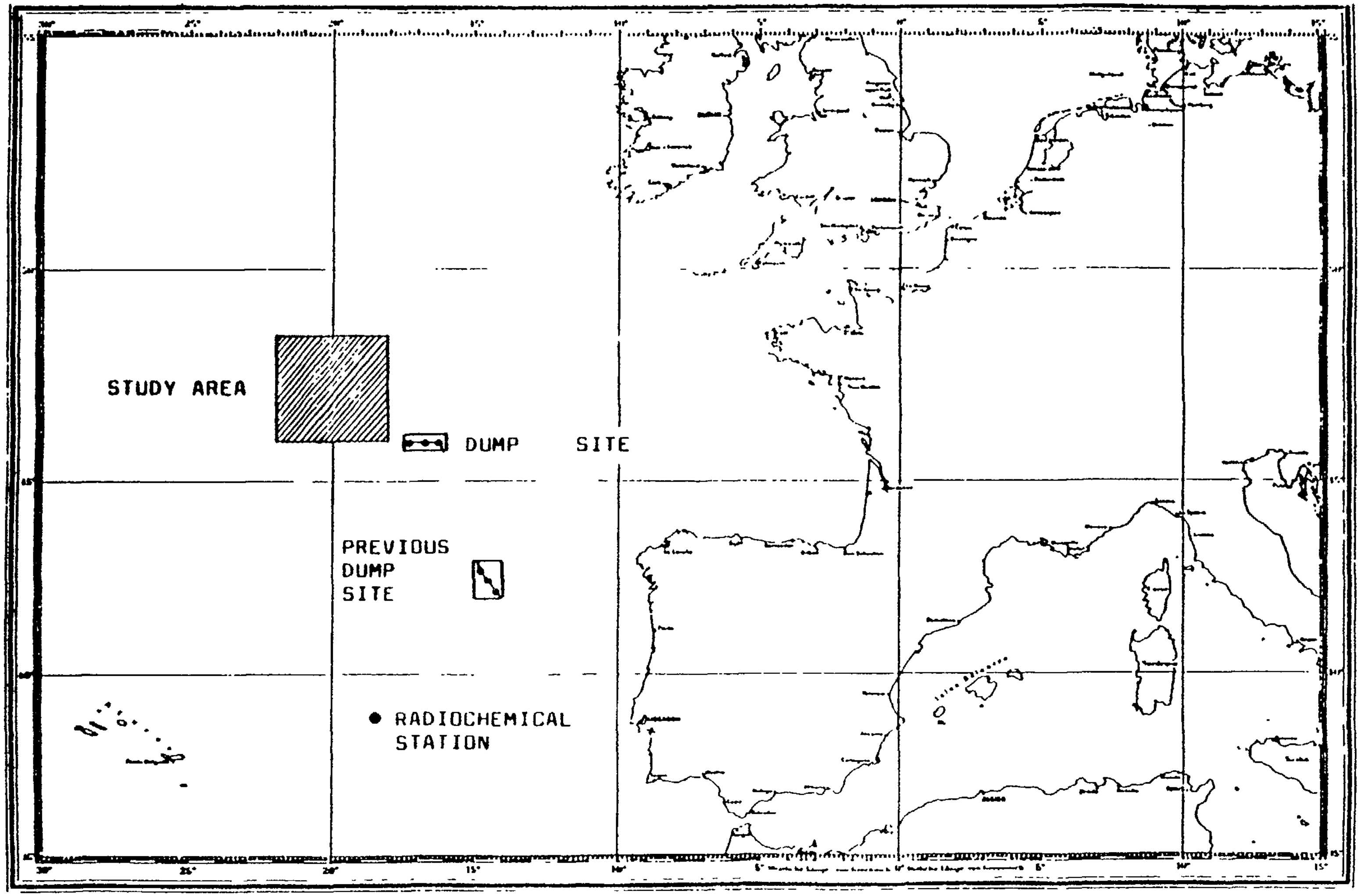


Fig. 1 The NOAMP area (hatched) and the actual and previous NEA dump sites

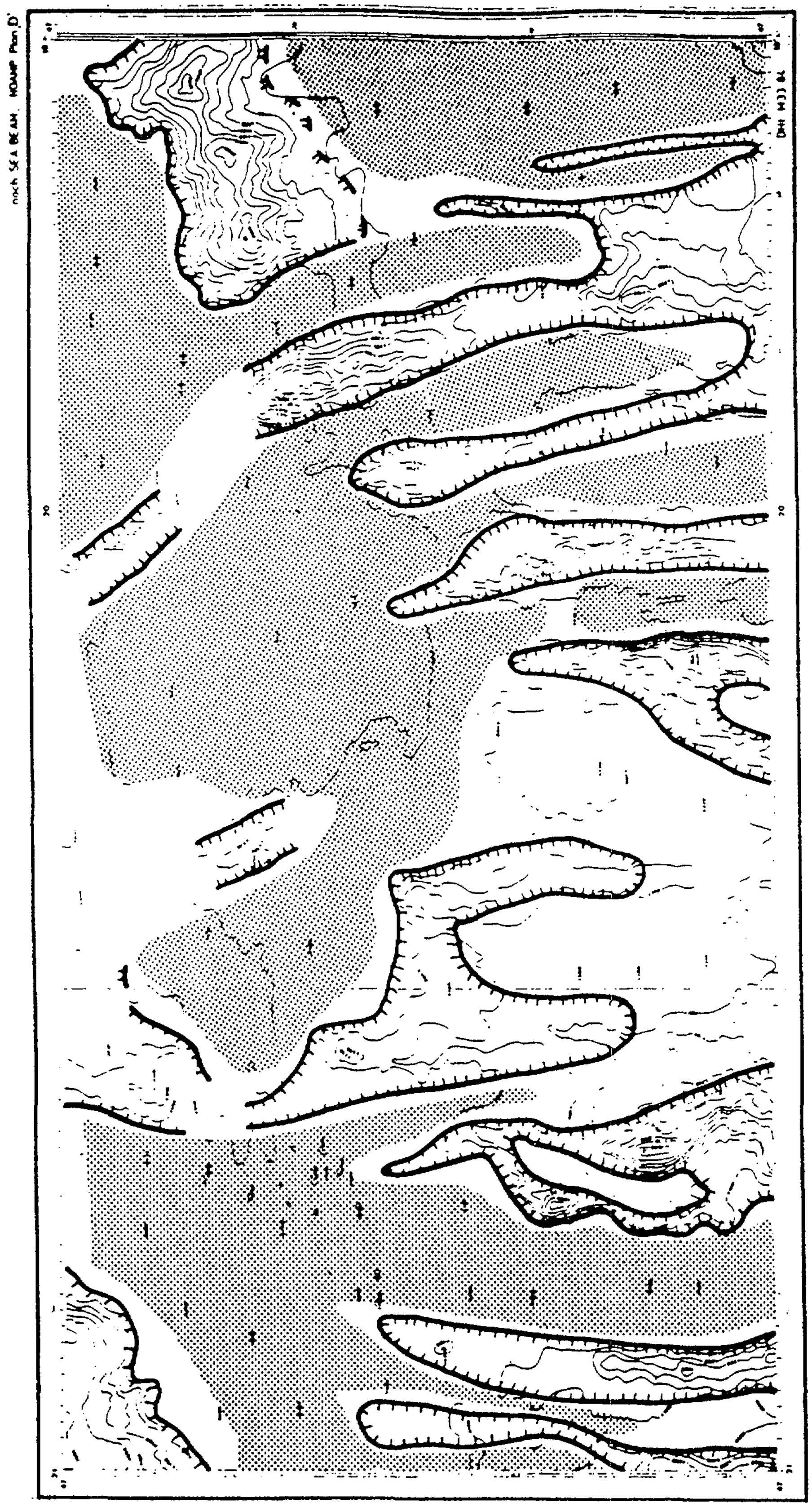


Fig. 2 Oceanic basement ridges (heavy lines) and valleys (shaded) in the central NOAMP box

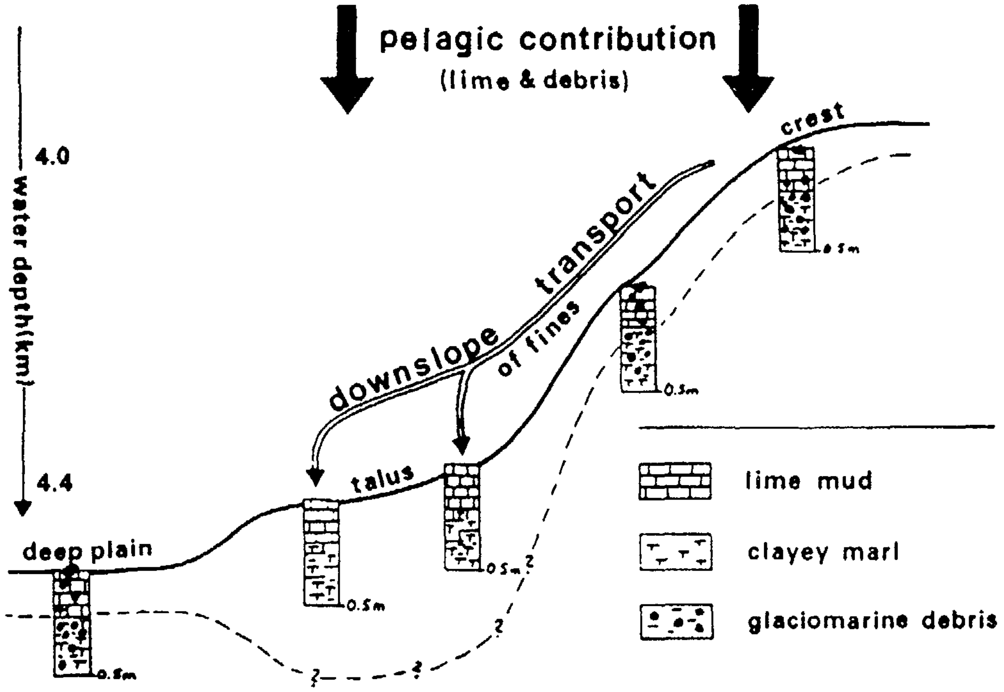


Fig. 3 Schematic model of the sedimentation and sediment transport at a deep sea hill.
A possible mechanism for down-slope transport might be winnowing by currents.

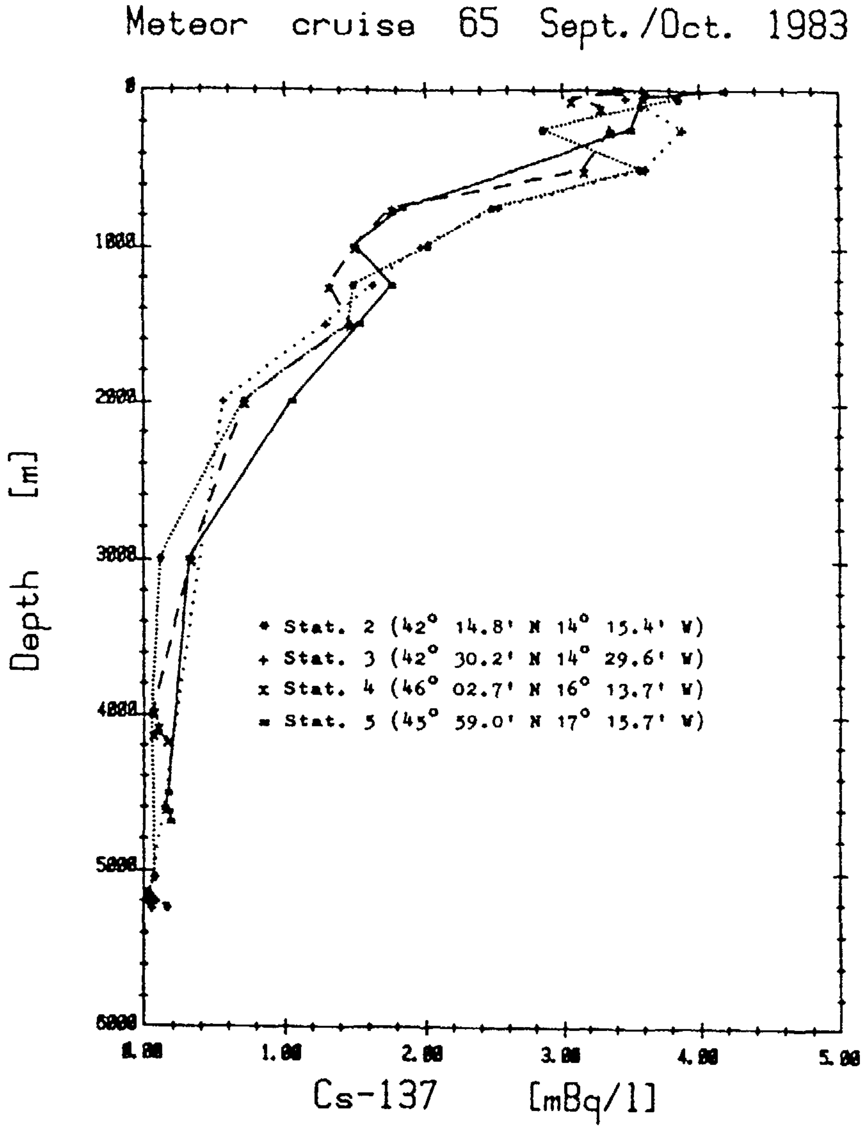


Fig. 4 Vertical profiles of the ^{137}Cs activity concentration in the water column of the previous (Stat. 2 and 3) and the actual (Stat. 4 and 5) NEA dumpsites in the North-East Atlantic.

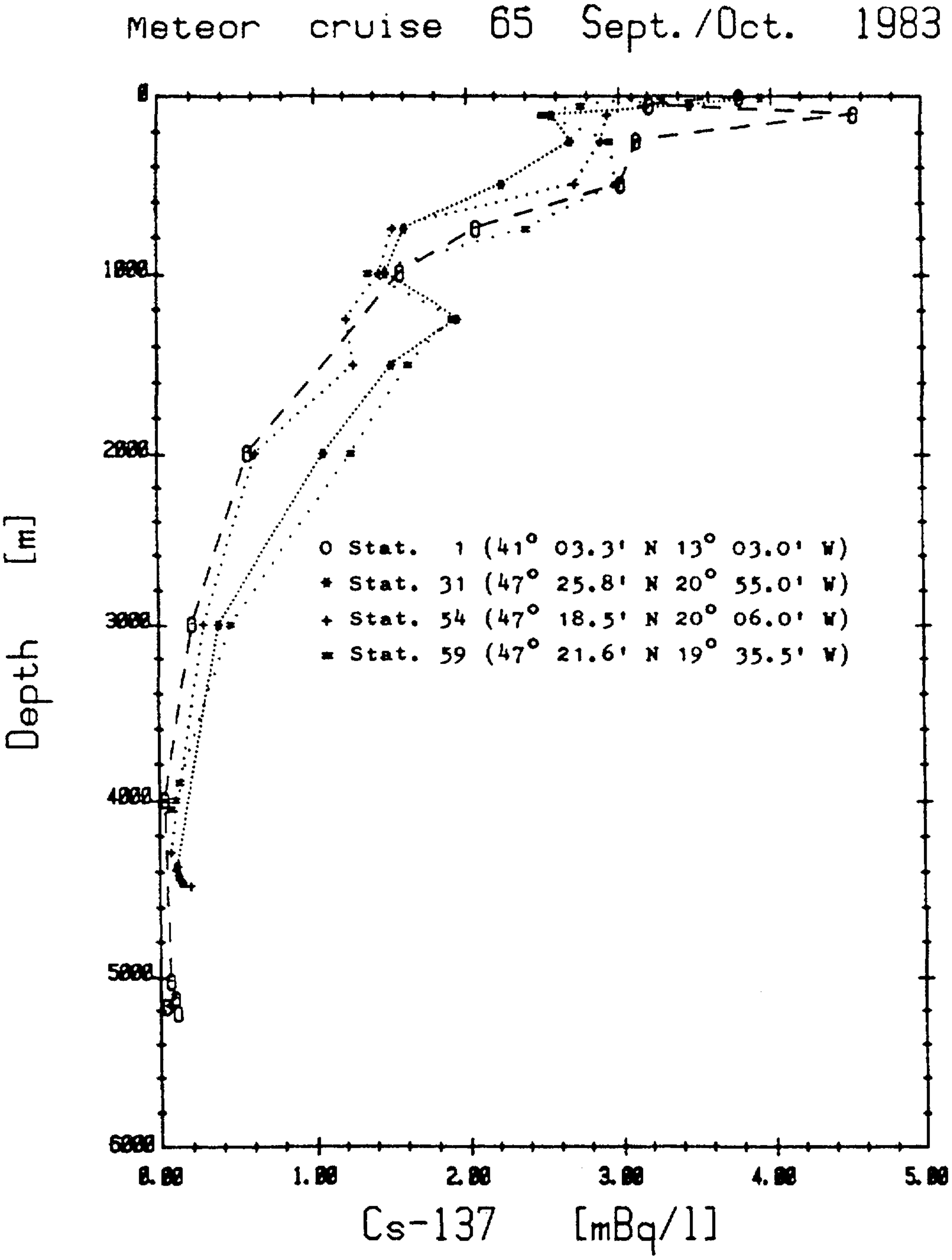


Fig. 5 Vertical profiles of the ^{137}Cs activity concentration in the water column at reference locations

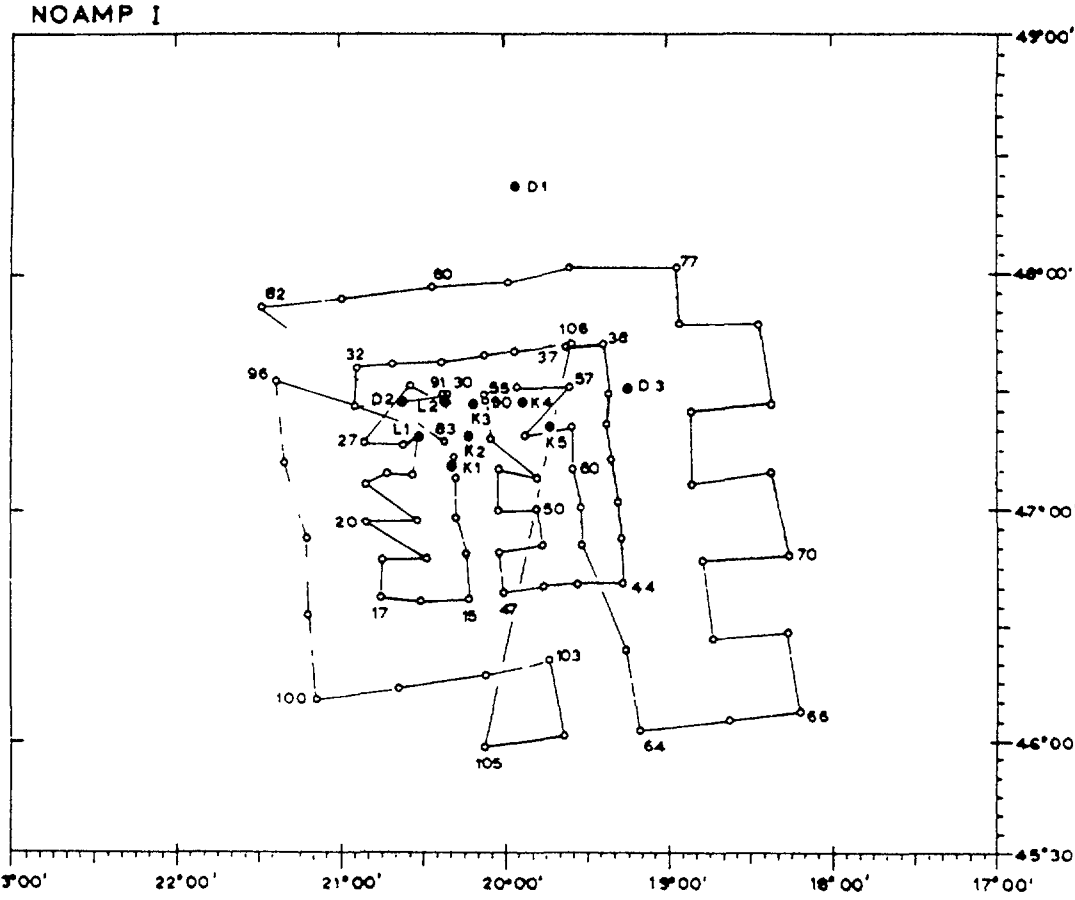


Fig. 6 Station grid during NOAMP I
o CTD-Stations
● Current metre moorings; D1, D2, D3 are COB (Brest)-moorings

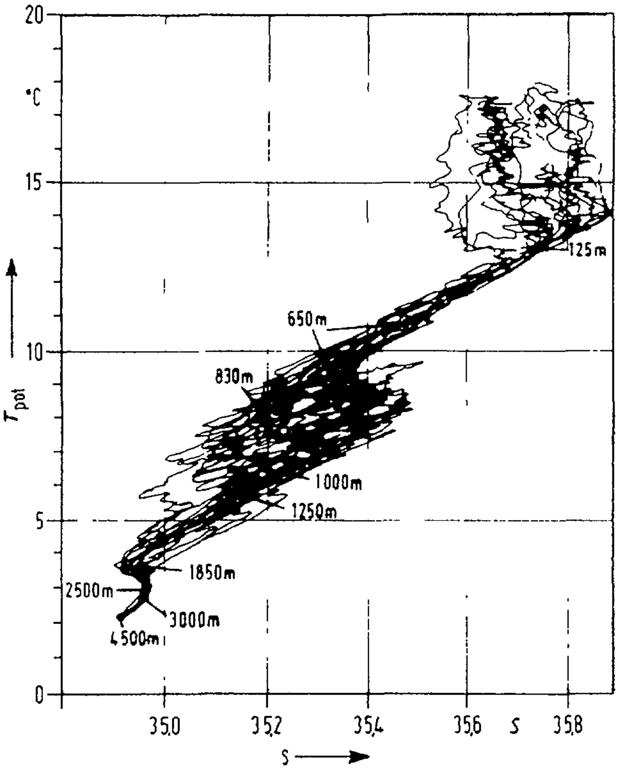


Fig. 7 Potential temperature/salinity-diagram from NOAMP I (uncorrected raw data)

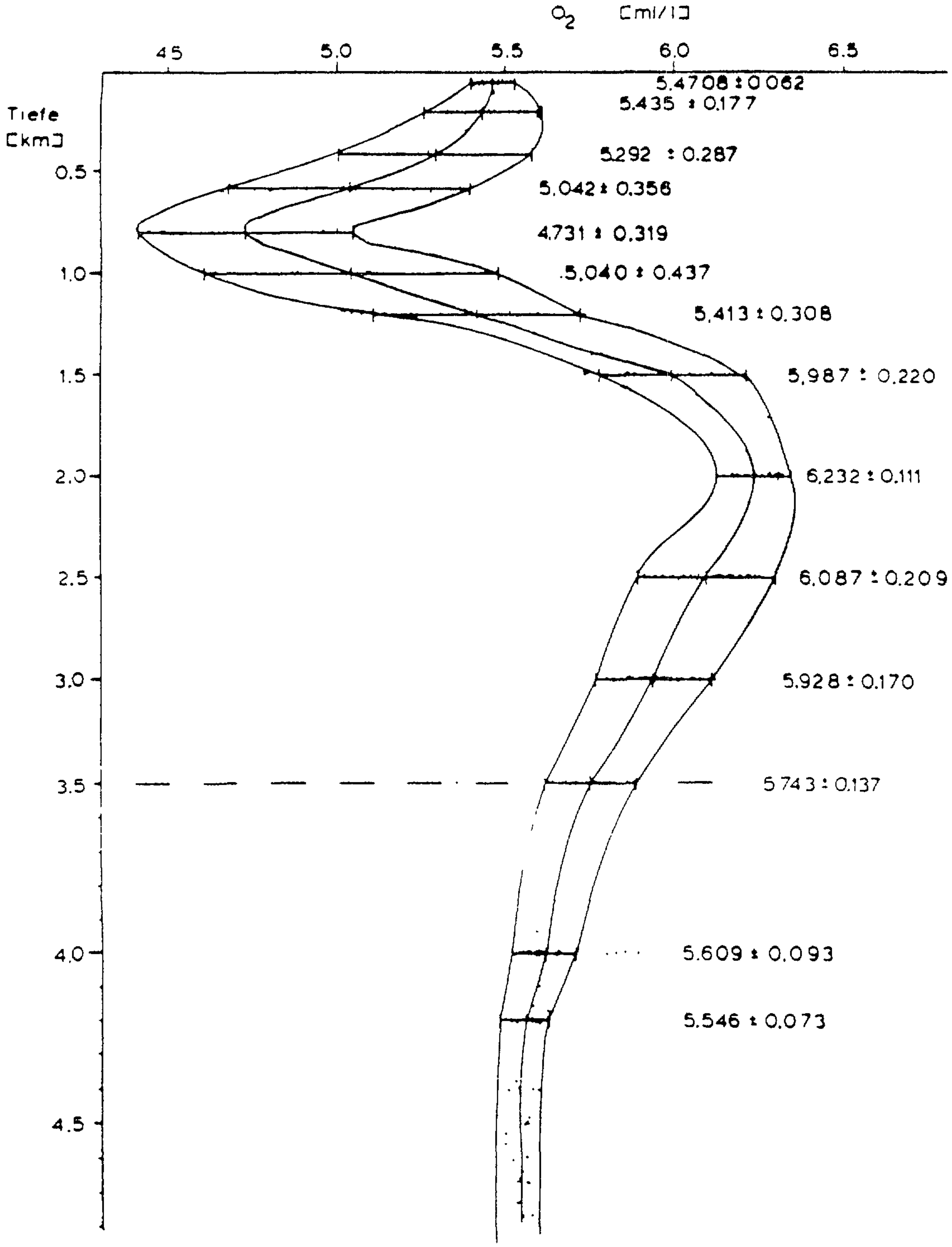


Fig. 8 Scatter range of the vertical O_2-profile
Composite of all O_2-determinations during NOAMP I
Bars indicate standard deviation.

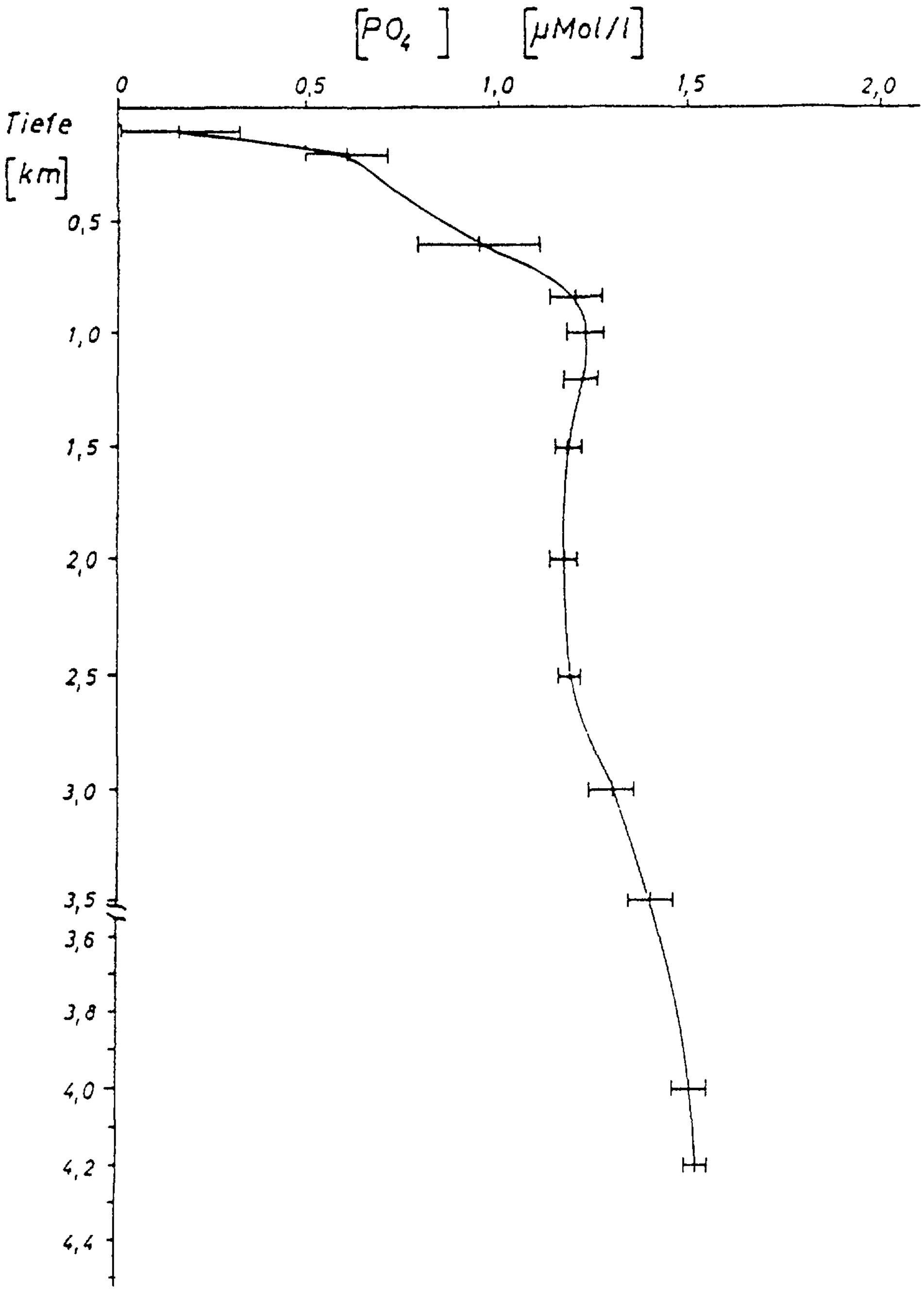
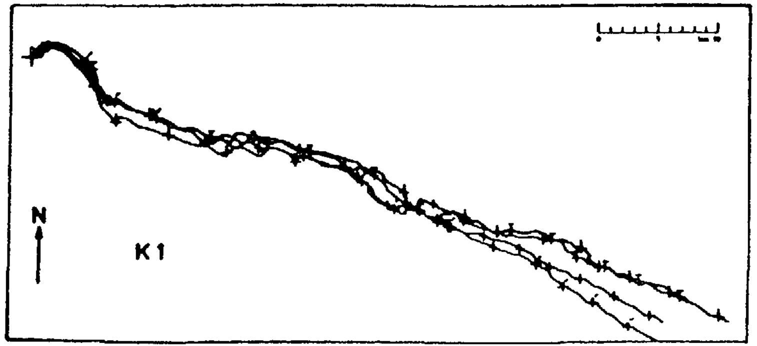
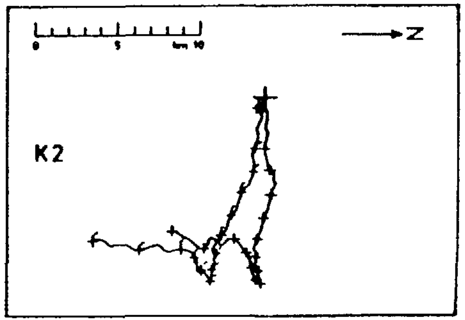


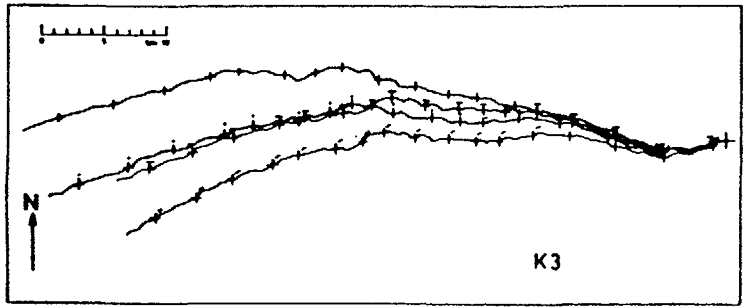
Fig. 9 Vertical profile of PO_4 with scatter bars Composite of all PO_4-determinations during NOAMP I

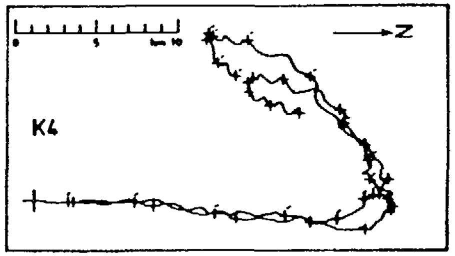
Bars indicate standard deviation.

Fig 10 Mean current vectors, averaged over about 17 days during NOAMP I
Observation depths: 10, 30, 70, 150, 200, and 250 m above the bottom
Sampling interval: 5 minutes
Isobaths in meters









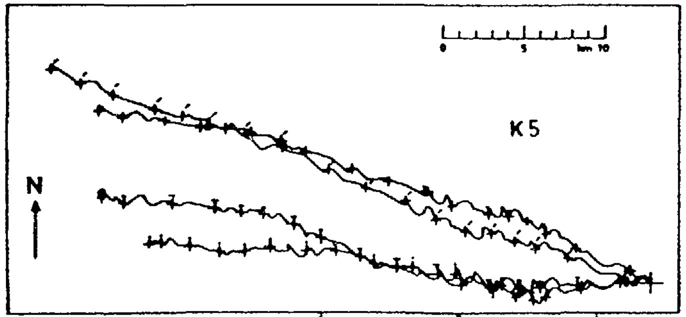
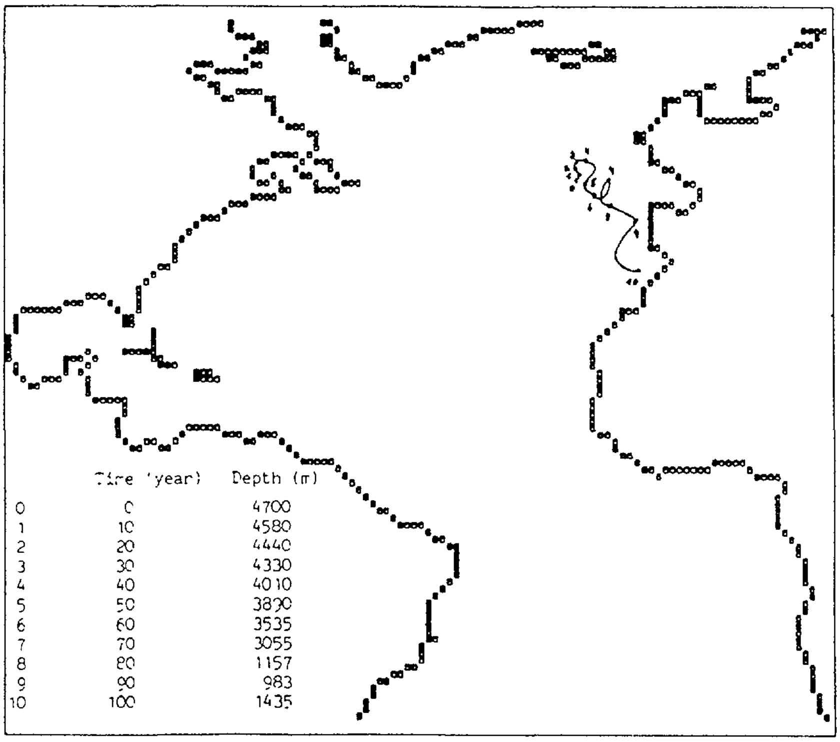
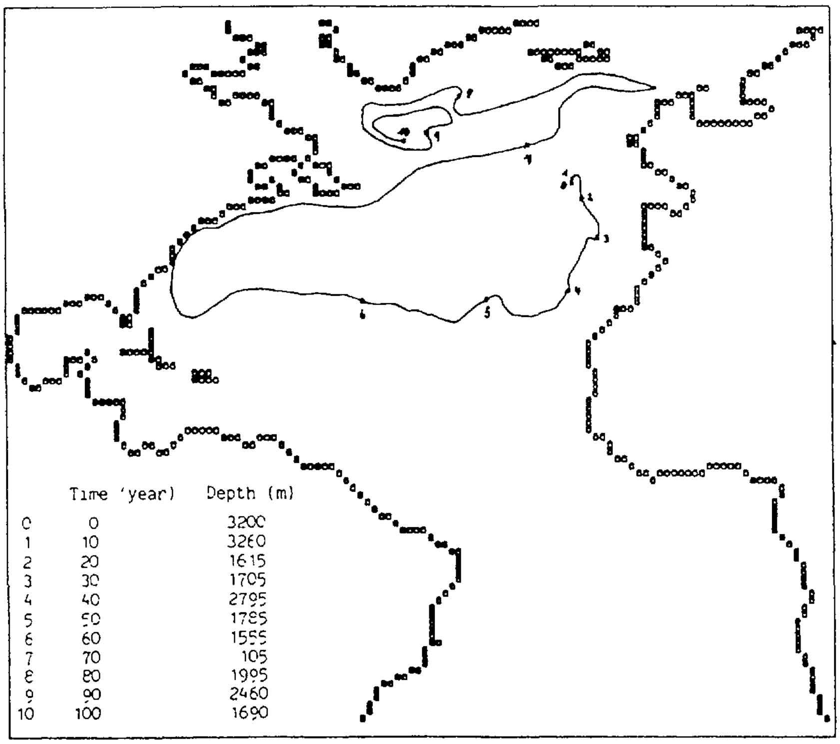


Fig. 11 Unfiltered progressive vector diagrammes within a 300 m thick layer above the bottom during NOAMP I
Different trajectories in one diagramme indicate different observation depths
Crosses indicate 24 h-intervals
Duration: about 17 days
Location of the position K1, ... K5, see Fig. 9.



	Time (year)	Depth (m)
0	0	4700
1	10	4580
2	20	4440
3	30	4330
4	40	4010
5	50	3890
6	60	3535
7	70	3055
8	80	1157
9	90	983
10	100	1435

Fig. 12 Three-dimensional trajectory of an advected particle 100 years after being released at a depth of 4700 m in the NOAMP area.
The trajectory is annotated at 10 year interval.
The consecutive numbers at the trajectory indicate the position and the depth of the particle every 10 years (see table on the left).
The source is at 0.



	Time (year)	Depth (m)
0	0	3200
1	10	3260
2	20	1615
3	30	1705
4	40	2795
5	50	1785
6	60	1555
7	70	105
8	80	1995
9	90	2460
10	100	1690

Fig. 13 Three-dimensional trajectory of an advected particle 100 years after being released at a depth of 3200 m in the NOAMP area.
The trajectory is annotated at 10 year interval.
The consecutive numbers at the trajectory indicate the position and the depth of the particle every 10 years (see table on the left).
The source is at 0.

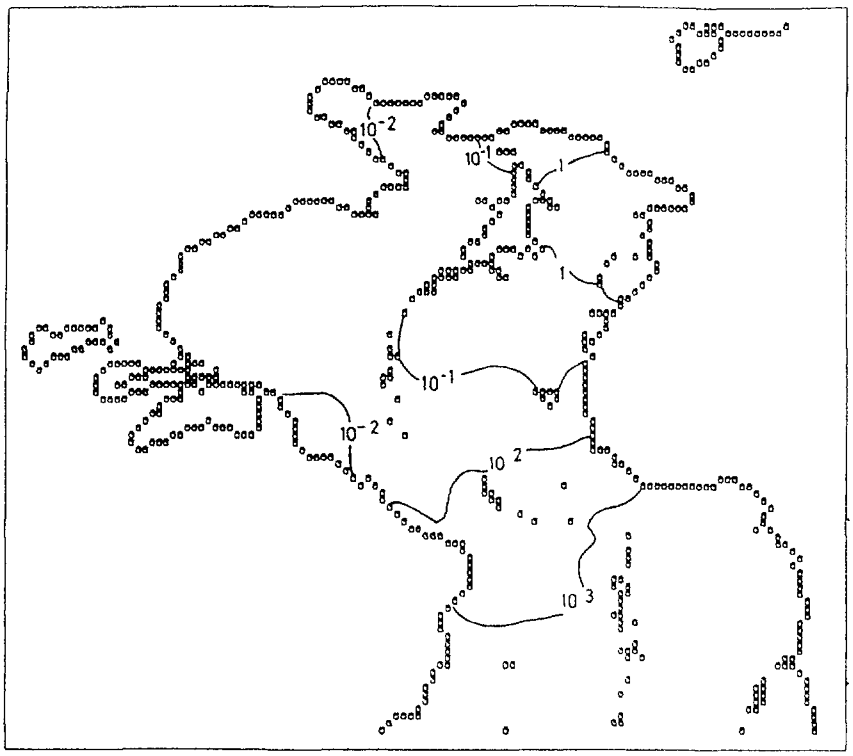


Fig 14 Concentration of activity (Bq/m^3) at 3000 m depth, 100 years after continuous release of 1000 TBq/year.
The source is at a depth of 4500 m in the NOAMP area
Diffusion coefficients $A_H = 10^7$ cm^{2}s^{-1} and $A_V = 1$ cm^{2}s^{-1}.

The concentration refers to a half life of 30 years
The small squares denote the 3000 m depth contour

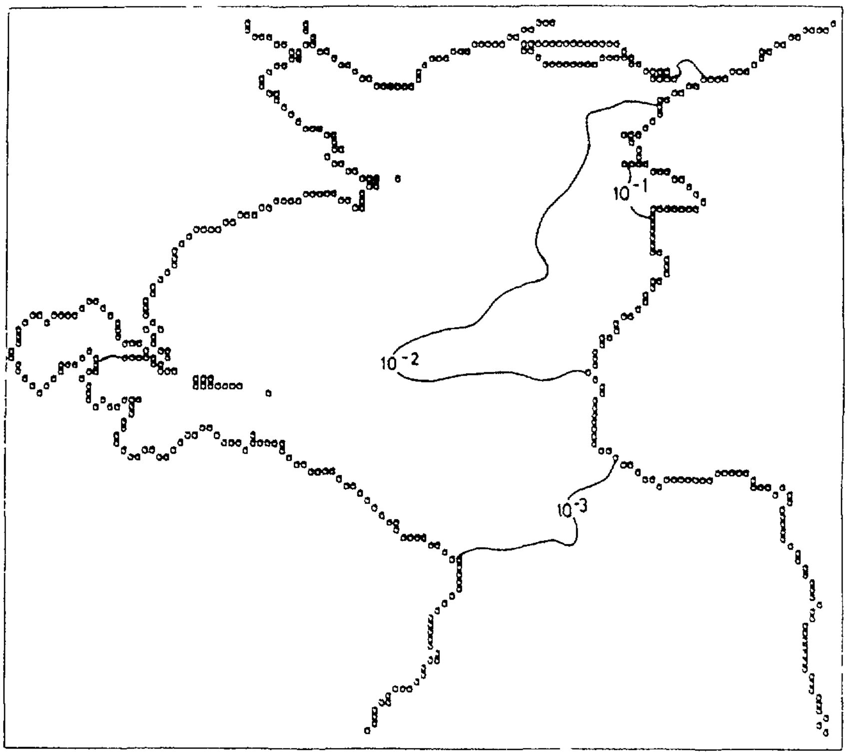


Fig.15 Concentration of activity (Bq/m^3) at a depth of 500 m,
100 years after continuous release of 000 TBq/year
The source is 4500 m depth in the NOAMP area.
Diffusion coefficients: $A_H = 10^7$ cm^{2}s^{-1} and $A_V = 1$ cm^{2}s^{-1}

The concentration refers to a half life of 30 years

The small squares denote the 500 m depth contour

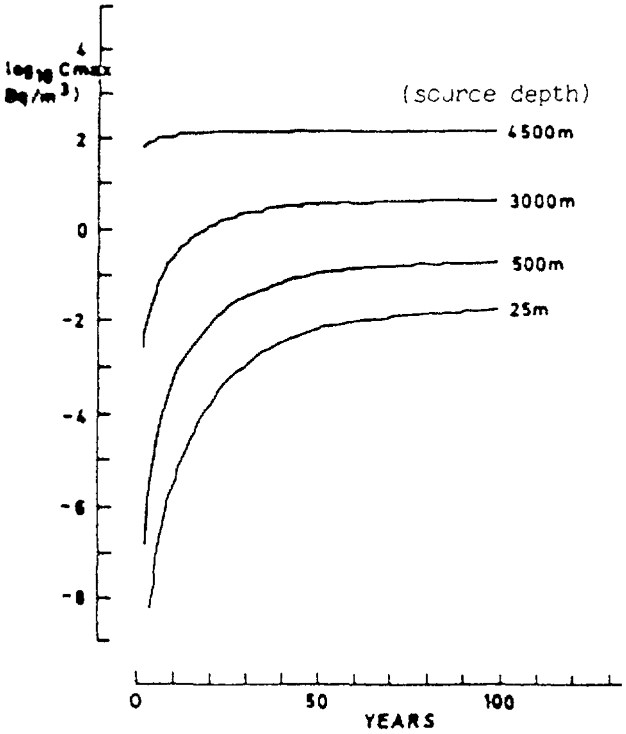


Fig. 16 Temporal adjustment of the maximum concentration of activity in $\log_{10} C_{max}$ (Bq/m^3) at 4500, 3000, 500 and 25 m Tiefe during a continuous release of 1000 TBq/year at 4500 m depth. Diffusion coefficients: $A_H = 10^7$ cm^{2}s^{-1} and $A_V = 1$ cm^{2}s^{-1}.
The concentration refers to a half life of 30 years.

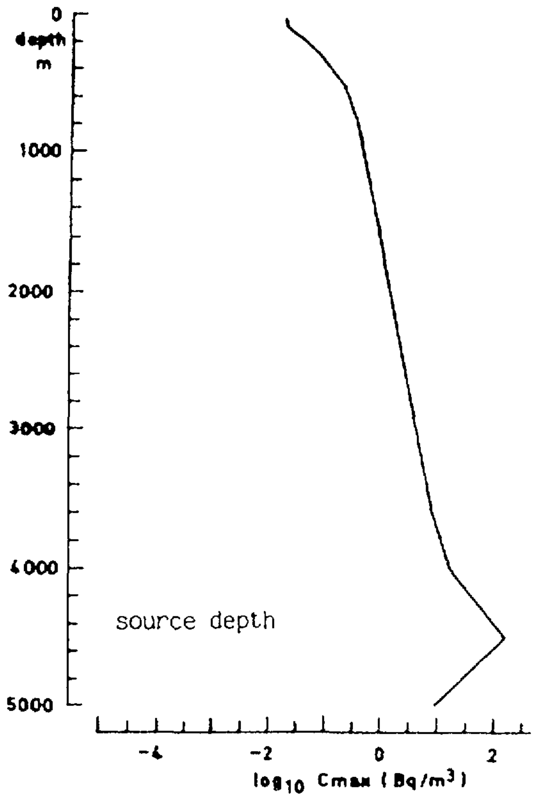


Fig. 17 Maximum concentration of activity in $\log_{10} C_{max}$ (Bq/m^3) as function of depth (m) after 100 years of continuous release of 1000 TBq/year at 4500 m depth.
Diffusion coefficients: $A_H = 10^7$ cm^{2}s^{-1} and $A_V = 1$ cm^{2}s^{-1}
The concentration refers to a half life of 30 years.

THE BEHAVIOUR OF CERTAIN LONG-LIVED RADIONUCLIDES IN THE MARINE ENVIRONMENT*

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Abstract

Methods have been developed for analysis of ^{99}Tc, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, ^{230}Th, ^{234}Th, U nuclides in fish tissue and different oxidation states of Pu, Am and Np. Research, much in the Irish Sea has studied the latter elements and Tc and provided information about distribution and speciation in water. Pu isotope ratios give information on the source (Sellafield, Cap La Hague, or fall-out). The possibility of memory effects in shipboard sampling systems is pointed out. At least 240 TBq of ^{239,240}Pu and 290 TBq of ^{241}Am are associated with the upper 30 cm of the seabed within a 30 km belt of the Cumbrian coast. Bioturbation has been studied using ^{14}C, ^{210}Pb, ^{234}Th, Pu, Am, Cm and redistribution down to 140 cm demonstrated. Pu and Np isotopes were partially reduced in interstitial water and the presence of artefacts due to subsequent exposure to oxidising conditions was shown to be important, and to be avoided. Organic complexation is also being studied. Concentration factors for many of the above isotopes in biota were derived. A review of K_d factors for deep sea environments was produced.

1. Introduction

Many of the long-lived radionuclides associated with the deep-sea disposal of radioactive waste are released into UK coastal waters, principally from the British Nuclear Fuels plc reprocessing plant at Sellafield bordering the Irish Sea. The environmental behaviour of these nuclides is being studied primarily to assess the long-term consequences of coastal water discharges, but the Irish Sea also provides unique opportunities to study certain aspects of *in situ* radionuclide behaviour which cannot be achieved in the deep sea environment. It also needs to be borne in mind that a large fraction

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of the dose to man resulting from any disposal of radionuclides into the deep sea will arise via coastal water pathways. Direct studies on deep sea materials have also been made, however, plus research on physical and chemical oceanographic processes which may influence the behaviour of radionuclides released in the deep ocean.

Much of the deep-sea programme has involved studies of processes at the Nuclear Energy Agency (NEA) low-level radioactive waste dumpsite in the NE Atlantic because of the UK's active involvement in packaged-waste disposal at this site in recent years ([1-19]).

2. Methodology

A considerable effort has been spent on developing and improving the analytical methodology. A method suitable for the separation of Tc from water, sediments and biota has been developed and successfully tested in an international intercomparison exercise organised by the US Dept. of Energy. (M. S. Feiner, 1984. A ^{99}Tc vegetation reference material. Environ. Measurements Lab. US Dept. Energy, New York, 27 pp.) It consists of an initial ammoniacal ashing at 450°C (where appropriate), a ferric hydroxide scavenge from chloride solution to remove many contaminating radionuclides, followed by the uptake of pertechnetate on to an anion exchange column from NaOH solution. Tc is removed from the column with $NaClO_4$ and finally co-precipitated with CuS prior to β counting for ^{99}Tc. Work is being carried out to investigate the suitability of ^{99m}Tc, ^{95m}Tc and ^{97}Tc as yield tracers. A discussion of the use of yield tracers in the determination of alpha-emitting actinides has been published([20]).

The techniques developed for the measurement of ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, ^{230}Th and ^{234}Th in samples of seawater, sediment and biological tissues have been described with some examples of the data produced([21,22]). Further refinements to the method of detection of ^{234}Th in sediments are being made.

A technique for the analysis of uranium nuclides in fish tissue at environmental levels has been developed. Processing blanks of ~ 0.1 mBq kg^{-1} (wet tissue) have been achieved by using non-glass apparatus and isolating U as U(IV). The latter precaution avoids the need to use chemicals, for the separation of U as U(VI), which invariably contain U as a contaminant.

In order to differentiate between the two higher oxidation states of Pu (V and VI) in seawater, a technique involving co-precipitation on Ca-CO_3 at pH 9.0 by the addition of a $Na_2CO_3/NaHCO_3$ mixture has been investigated. Approximately 80% of Pu V will co-precipitate under these conditions. Less than 10% of Pu VI co-precipitates, as can be demonstrated by carrying out a replicate co-precipitation having made the seawater 0.001M with respect to $KMnO_4$, which maintains any 'oxidised' Pu in the hexavalent state. Preliminary results indicate that the Pu is predominantly in the pentavalent form.

An investigation has also been made of $Fe(OH)_3$ (0.1 mg Fe l^{-1}) as an alternative co-precipitant for reduced forms of the transuranic elements. Both this and the NdF_3 method gave similar results for Pu. But some 20% of the environmental ^{241}Am in seawater failed to follow the ^{243}Am(III) yield tracer in the hydroxide precipitation. This figure increased to 70% in some waters with higher suspended loads (> 5 mg l^{-1}). It appears that another form of Am is present which subsequently can be quantitatively scavenged on to $Fe(OH)_3$, using ^{242}Cm(III) as a yield tracer, following the addition of a reducing agent (Na_2SO_3 at pH 1.0). Work is continuing to identify the second Am species or complex.

A reliable ^{235}Np tracer has been produced and used to study the co-precipitation of Np in different oxidation states, both by the NdF_3 and $Fe(OH)_3$ (0.1 mg l^{-1}) methods, and with Ca as $CaCO_3$. Laboratory experiments in an ultra-violet irradiator indicate an equilibrium between the two oxidation states which is pH dependent (Fig. 1).

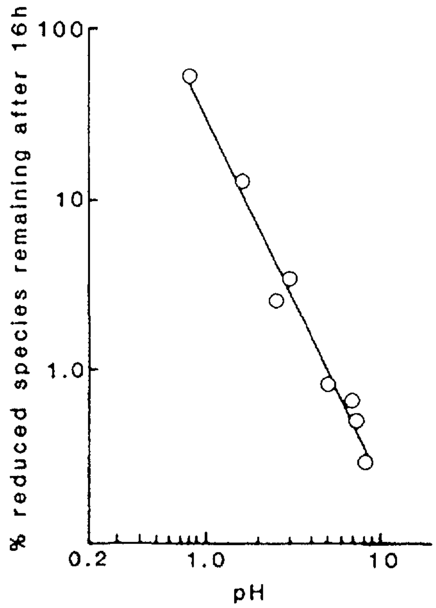

Fig. 1 Oxidation of ^{235}Np tracer in a U.V. irradiator. HCl and NaOH added to 800 ml seawater to adjust pH.

Routine quality control is applied to all analytical procedures; for Pu and Am the vast range of concentrations in samples handled (> 10^7) creates potential problems of cross contamination, but blank levels over the whole range are kept below 1%, and are typically 0.1%, of the sample concentrations. The laboratory takes part in both national and international intercomparison exercises; the results of a recent one of U are given in Table 1. It should be noted, however, that 'concensus values' do not necessarily represent the 'true' concentrations. A number of certified reference materials are now available, but even these offer little help in detecting analytical bias at the lowest concentration levels. Ultimately, confidence arises from continued intercomparison of results. As an example, Table 2 indicates the concentrations and Pu nuclide quotients of sea water samples collected in the Arctic Ocean. Differences in the quotients - from those of fallout to those associated with coastal water discharges - indicate the ability to detect these nuclides to a high degree of accuracy and precision.

Table 1. Recent Intercalibration Exercises

Nuclide	FRL data $Bq.kg^{-1}$	Mean value of all participants $Bq.kg^{-1}$	Range of values $Bq.kg^{-1}$
(a) Uranium nuclides in a marine sediment (acid leach)			
^{238}U	15.28±0.63	14.07±2.22	11.48-16.42
^{234}U	16.10±0.62	14.37±2.07	11.43-16.10
$^{234/238}$ RATIO	1.05±0.06	1.02±0.07	0.94- 1.08

(b) ^{237}Np in a marine sediment

	FRL data $Bq.kg^{-1}$	Mean value of all participants $Bq.kg^{-1}$	Range of values $Bq.kg^{-1}$
	6.25±0.12	6.22±0.29	5.92-6.60

Table 2. Americium and plutonium in filtered seawater CIROLANA cruise from the North Sea to the Arctic 1981

Station number	Latitude	Longitude	^{241}Am $\mu Bq.1^{-1}$	$^{239+240}Pu$ $\mu Bq.1^{-1}$	^{238}Pu $\mu Bq.1^{-1}$	$\frac{^{239+240}Pu}{^{238}Pu}$
2	54°N	1°E	2.29±0.14	44.9± 2.1	9.22±0.46	4.9±0.1
10	58°N	4°E	1.46±0.08	19.4± 0.8	2.68±0.13	7.2±0.2
32	67°N	10°E	1.62±0.11	16.3± 0.8	1.79±0.12	9.1±0.5
106	74°N	10°E	1.86±0.13	13.7± 0.6	0.87±0.06	15.8±1.0
123	80°N	7°E	1.89±0.17	15.4± 0.7	0.85±0.07	18.2±1.3
140	72°N	6°W	2.46±0.18	12.6± 0.6	0.60±0.06	21.1±1.8
166	64°N	0°	1.58±0.11	4.74±0.22	0.44±0.04	10.8±0.9
181	58°N	0°	2.39±0.27	49.1± 2.1	9.92±0.53	4.9±0.2

Errors quoted are ± 1σ propogated counting errors only

3. Shelf seas research

Measurements have been made of the chemical nature of the effluent discharged from the BNFL reprocessing plant at Sellafield, UK([23,24]). The effluent arises both from water used to purge fuel element ponds and miscellaneous sources routed through 'sea tanks'. The latter is the major source of transuranium elements (> 90% for Pu(α)). A large proportion of the Pu(α), ^{241}Am, $^{243/244}$Cm and ^{237}Np was associated with particulate (> 0.22 μm) material which also contained 'hot' particles, identified as discrete clusters of α tracks by CR-39 α-track detection. Both Pu(α) and ^{241}Am were solubilised on dilution (1:10^4) in seawater and there were corresponding changes in oxidation state([24]).

The distribution and speciation of Tc, Np, Pu and Am have been investigated on a number of cruises throughout UK coastal waters. No evidence has been found so far for a reduced form of Tc in the Irish Sea. Most Np is present as Np(V) but a small proportion (0.2-0.3%) is present as Np(IV), consistent with the pH-dependent equilibrium reaction investigated experimentally with ^{235}Np (Fig. 1). Measurements of Np have been made in all UK coastal waters. The discharge from the Cap de la Hague reprocessing plant is clearly superimposed on the distribution pattern of Sellafield-derived Np (Fig. 2). K_D values for Np between suspended particulate and seawater (1 E3-7 E4) were similar to those reported previously([25]). Further data have been obtained on the distribution and speciation of ^{238}Pu, $^{239/240}$Pu and ^{241}Am in filtered seawater and suspended particulate. The variation in Pu isotope ratios has been used to identify the sources of Pu as Sellafield, Dounreay (N. Scotland), Cap de la Hague or from fallout (Atlantic Ocean).

Seawater samples are usually collected using the ship's continuously-pumped seawater supply, which has an intake, 3 m below the surface, fitted with a zinc screen which acts as a sacrificial anode. It has been demonstrated, in the later part of 1984, that this sampling method results in a memory effect which becomes apparent when passing from waters with relatively high radionuclide concentrations to waters with relatively low radionuclide concentrations. This can result not only in anomalously high Np, Pu and Am concentrations, but also in erroneous K_D estimates. The magnitude of the effect is dependent upon the ship's location, and

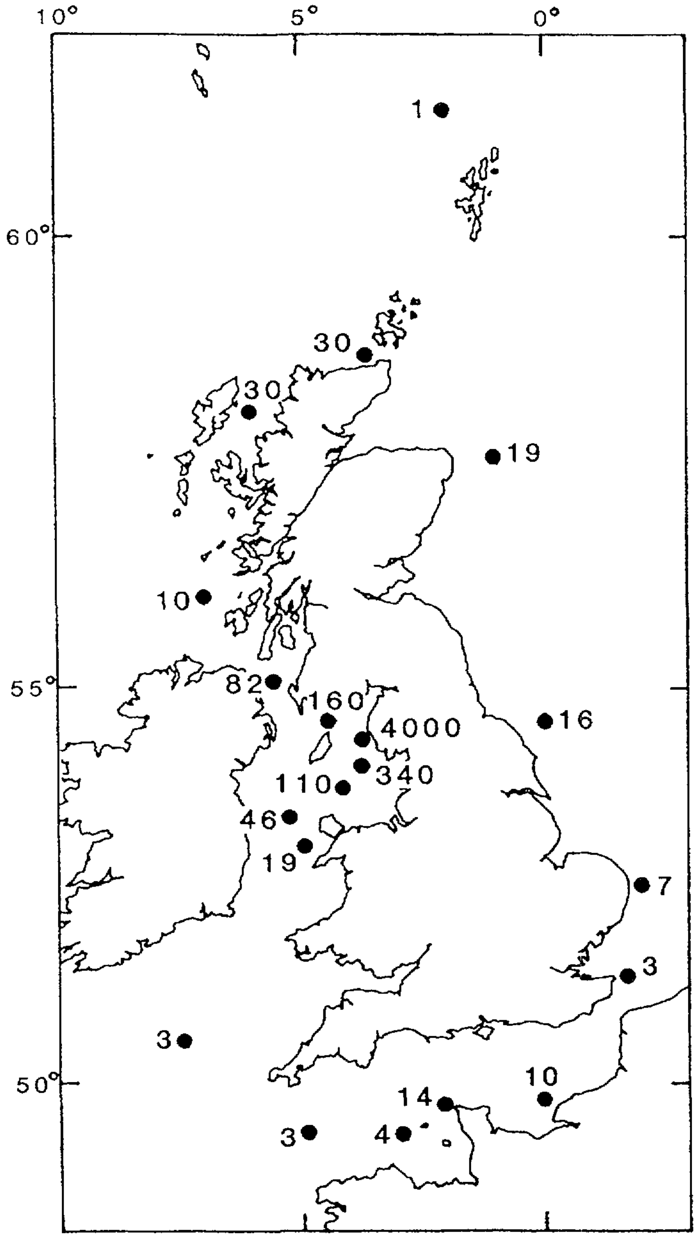

Fig. 2 Concentration of ^{237}Np ($\mu Bq\ l^{-1}$) in filtered seawater in UK coastal waters in 1982 and 1983.

the time spent at that location, in the period prior to sampling. A comparative study is being undertaken using alternative sampling techniques (e.g. Niskin bottles) and the results of this study, together with an assessment of the quality of previously collected data, will be reported in due course. Undoubtedly the most significant effect will be on samples collected in Atlantic waters (i.e. fallout levels) immediately after the ship has spent a prolonged period (several weeks) in the NE Irish Sea. The higher than expected ^{237}Np concentrations of 3 $\mu Bq\ l^{-1}$ measured in the SW Approaches in 1982 and 1983 (Fig. 2) almost certainly result from this memory effect. This case serves as a warning that problems concerning data quality may come from unexpected sources.

A considerable analytical effort has been expended to estimate the quantities of Pu and Am residing in the sediments and water of the Irish Sea. An inventory of Pu and Am, as of 1977/1978, has been published(23). At least 240 TBq of $^{239/240}$Pu and 290 TBq of ^{241}Am were associated with the upper 30 cm of the seabed within a 30 km wide belt along the Cumbrian coast. An extensive re-sampling programme has been carried out which will provide an improved inventory estimate, as of 1983, taking account of the observed vertical distribution of Pu and Am in the seabed(34).

The distribution of naturally-occurring radionuclides in Irish Sea sediments has been used to assess the extent, and quantify the rates of, physical processes which will influence the future behaviour of artificial radionuclides. ^{14}C data fail to show active sedimentation but reveal deep, homogenous mixing of the seabed over a period of hundreds or thousands of years(40). Mixing processes have been further studied using ^{210}Pb and ^{234}Th. Rapid turnover of the upper few centimetres (months) and upper few tens of centimetres (years) is a widespread phenomenon. Direct evidence of the biological control on Pu, Am and Cm redistribution at depths of up to 140 cm by bioturbation has been published(26,27). An extensive survey of the distribution, density and behaviour of benthic fauna has been undertaken. The large echiuroid Maxmülleria lankesteri and the crustacean Callianassa subterranea are regarded as the most important bioturbating organisms. [It is worth noting that echiuroids are also known to occur in deep sea sediments.]

The radiochemistry of interstitial waters has been studied on two cruises to the Irish Sea. The results of the first cruise in 1982 have been published(28). The data confirmed previously published work(25,29) on the proportions of Pu in higher and lower oxidation states. Partial reduction of Np(V) to Np(IV) was observed. Considerable precautions were taken on the second cruise in 1984 to exclude oxygen at all stages of the sub-sampling, squeezing and analysis procedure.

The necessity for the elaborate precautions used in 1984 was tested by comparing Pu data obtained using methods used previously in 1979 (see 25). Changes in oxidation state in response to post-collection redox changes, and enhanced scavenging of reduced Pu (III+IV) by the oxidation of ferrous iron, could both arise from processing samples in the normal atmosphere, resulting in changes in the observed sediment-interstitial water distribution coefficient (K_D). There were no significant differences in Pu K_D values for particular depth horizons obtained using the two methods. It appears that elaborate precautions to exclude oxygen may not be necessary for these particular sediments but further work is required to confirm this. The quality of the separation of Np(IV) using both NdF_3 and TTA/xylene was monitored with ^{235}Np as a tracer. The Np data from this cruise are still being worked up. Some measurements were made of ^{241}Am which indicated a distribution coefficient between solid and liquid phases of about 1 E6.

The nature of sediment-radionuclide interactions in Irish Sea sediments is under investigation. Alpha-emitting 'hot' particles have been identified in surface and sub-surface sediments using the CR-39 (plastic) nuclear track detector technique. The spatial distribution of 'hot' particles off the Cumbrian coast approximates to that of $^{239/240}Pu$ measured by conventional α-spectrometry. Experiments are underway to examine the partitioning of Pu and Am between different components of the sediment, such as carbonate and Mn-oxide phases, by a sequential leaching procedure. Humic substances have been extracted from sediments and interstitial waters from the Irish Sea, and from 400 ℓ seawater samples from around the UK coast. They will be analysed for Th, U, Np, Pu, Am, Cm and Tc to assess the extent of organic complexation. A project has begun to study the relationship between suspended sediment load and radionuclide concentration, and the shorewards flux of sediment-bound radioactivity using rig-mounted current meter, transmissiometer and water sampler arrays. This project will be developed over a number of years.

Studies on the accumulation of long-lived radionuclides by biological materials have continued with emphasis on food species eaten directly by man(30). Measurements of Np, Pu and Am have been made in a variety of marine organisms and algae collected from St Bees Head near the Sellafield discharge and at Balcary Point some 30 miles distant on the southern Scottish coast. Concentration factors for each species are broadly similar at the two sites. Lobsters (Homarus gammarus) have been collected over a two-year period, from locations near to Sellafield, at three monthly intervals and analysed for Pu, Am and Cm. Analyses are also being made for Np and Tc. The results to date confirm previous observations on the different metabolism of Pu and Am, with the former being preferentially accumulated by claw muscle and the latter by tail muscle. Observed $^{241}Am/^{239+240}Pu$ quotients in claw muscle ranged from 1.4 to 3.1, in tail muscle from 7.4 to 19.2. In contrast, the quotients for the principal routes of entry into the animals, the gut and the gill, ranged from 0.7 to 1.3 and 0.6 to 1.4 respectively.

Other environmental studies have covered a number of subject areas, including the species-specific affinity of ^{99}Tc for benthic algae, the response of benthic algae to variations in time of pulsed discharges of ^{99}Tc from Sellafield, concentrations of transuranium nuclides in plankton collected off Sellafield, Dounreay and Cap de la Hague, and the distribution of a number of radionuclides, including U, in coastal water fish species. Laboratory accumulation experiments have been conducted with ^{95m}Tc, ^{237}Pu and ^{235}Np to assess their assimilation, retention and distribution in lobsters (Homarus gammarus), Nephrops norvegicus, winkles (Littorina littorea) and plaice (Pleuronectes platessa). The effects of moulting on the accumulation of Tc by juvenile losbters have been studied in detail; the results have been prepared for publication(31).

4. Deep sea research

A provisional assessment of radiation regimes in the deep ocean environment has been published(32,33). Measurements have been made of ^{210}Po, ^{238}Pu, and $^{239/240}Pu$ in the deep-sea fish Coryphaenoides armatus.

Studies of sedimentary processes which may influence radionuclide scavenging in the deep sea have been concentrated at the NEA Dumpsite. Discussions of sedimentation and bioturbation processes based on ^{14}C and ^{210}Pb data have been published(35-37). The uptake of ^{237}Pu by calcareous NE Atlantic sediments has been studied(28). A review of K_D and CF values for use in generic models of deep sea radioactive disposal has been prepared(38). The sorption properties of the NEA Dumpsite sediments and the K_D values used for the 1984 NEA Site Suitability Review have been discussed(39).

5. Conclusions

A considerable amount of data on the behaviour of long-lived radionuclides in UK coastal waters has been generated in the period 1982-1984. An understanding of the environmental behaviour of such radionuclides is required to allow accurate predictions to be made of the consequences of the deep sea disposal of radioactive wastes. Concomitantly, a knowledge is required of the physical and chemical oceanographic processes which will influence the migration of radionuclides released into the deep ocean.

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BIOLOGICAL MIXING AND RADIONUCLIDE REDISTRIBUTION IN MARINE SEDIMENTS*

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Abstract

Literature survey indicates that bioturbation strongly affects the recycyling of radionuclides through the benthic boundary layer, and nuclides such as $^{239,240}Pu$ and ^{241}Am may be resolubilized by anionic complexers released by fauna.Transfer of nuclides to fauna which ingest particles is very low, whereas transfer from water is much more efficient. This suggests that interstitial water is probably the predominant source of transuranics for benthic organisms in sediments.

Biological activities such as feeding, burrowing, and irrigation of benthic infaunal organisms clearly affect physical and chemical properties and characteristics of the sediment-water interface.This process of biological mixing or bioturbation of surface sediments is widespread and considered to be a possible important mechanism for the migratory behaviour of long-lived radionuclides in marine sediments (1).

In the geobiochemical cycling of many natural and man-made contaminants sediments may be considered as a final sink and/or ultimate pollutant reservoir in the marine environment. In addition to physical processes,bioturbation, generated by biological activties of sediment-dwelling organisms, seems to be a principle mechanism in transfers and recycling of sediment-associated pollutants through benthic ecosystems.

Among the sediment infauna deposit- and detritus-feeders are the most important and abundant groups that redistribute contaminants and radionucides from sediments to the overlying water, where other benthic organisms of the benthic boundary layer (2) are responsible for their vertical transport from deep to surface waters.

The extensive biological reworking of the sediment column, generally results in the disruption of the sedimentary stability and composition evidenced by a disturbance of the stratigraphy of the upper sediment layers, which normally are inhabited by more than 90 percent of meio- and macrofaunal species (3, 4).

Population densities of the sediment infauna show great variabilities in relation to physical and chemical characteristics of the sediment like grain size, organic matter content, oxygen content, compactness of the sediment etc (5). Besides these, other parameters such as depth and distance from the continent clearly influence benthic faunal densities, showing

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* Contribution N° 2197 of the CEC Radioprotection Programme.

a general decrease of population densities from about 10^3 in coastal environments to some tens or hundreds of individuals per square meter in the abyssal sea (6). The most abundant species found were Polychaetes, Crustacea, Pelecopoda and Sipunculoidea which comprise 80 to 100 percent of the fauna. Generally, the importance of the meiofaunal taxa in this context is clearly underestimated due to difficulties of quantitative sampling procedures. Nevertheless, these groups may be found up to 4 times more abundant than the macrofaunal taxa with nematodes as the dominating group (7).

In the process of biological reworking of sediment particles, biological mixing or turnover rates of sediments have been reported to reach values of 10^2 to 10^6 cm^2/1000 years for densely populated, coastal environments, whereas these rates decreased with depth to 1 to 10^3 cm^2/1000 years in the deep ocean reflecting reduced biological activities (8). Sediment turnover rates induced by bioturbation may vary considerably from once every 15 years to once every 10 weeks according to species involved and the population densities present. However, most rates fall in the range of 1 to 5 years typical for populations of deposit-feeding polychaetes. The annual rate of sediment turnover for polychaetes from the continental slope (250 m) was reported to be about 10 Kg dry sediment/m^2/year. Assuming a medium sediment reworking depth of 5 cm (5×10^4 ml sediment/m^2), a steady state population of polychaetes could completely turnover the sediment in 4 to 5 years (9). In shallow areas, however, it is not surprising to find that the surface of the muddy sea floor is passed through the benthos at least once, and in some cases, several times a year (5).

The amount of organic matter in sediments can affect sediment turnover rates, which, as a consequence, decrease with increasing food supply. Deposit- and suspension-feeders entrap biological particles from the water column and the sediment, aggregate the ingested material in the gut, and void the feces as discrete pelletes or fecal strings. This process of biodeposition is known to be important to biogeochemical cycles especially in intertidal areas. Deposit-feeders probably play the quantitatively most important role in "pelletizing" marine sediments by biodeposition of feces and pseudofeces. In some areas between 40 to 100 percent of the particles of the sediment surface are in the form of pellets mainly produced by polychaetes and bivalves, sometimes resulting in an upper, 1 cm, thick surface layer of pellets (5).

The reworking of the sediment column by populations of deposit-feeding bivalves may reach values of 60 to 120 Kg sediment/m^2/year. This process accelerates the remobilisation and vertical transport of organic detritus together with nutrient-rich bottom mud to the sediment-water interface serverving, after resuspension into the water column, as a potential source of food for suspension-feeders, whereas the particles may act as scavengers for radionuclides with subsequent sedmentation and incorporation into the sediment.

Recent field data confirm, that bioturbation strongly affects the recycling of radionuclides through the benthic boundary layer especially in highly productive areas. The feeding activities of infaunal benthic organisms transfer radionuclides from the overlying water to the sediment (10). Pu-239, Pu-240 and Am-241 fixed in sediments may be resolubilized in the presence of anionic organic complexes, released deep in the sediment by metabolic activities of the infauna. In this form the radionuclides may freely migrate upwards through the sediment via interstitial waters or through infaunal borrows and finally could be released into the overlying waters.

Benthic organisms may play an important role in the redistribution of transuranium nuclides in near shore and deep-ocean sediments. In the benthic boundary layer Pu and Am, present in the water, will become readily associated with a variety of benthic fauna living in or on the sediment. Accumulation of transuranium nuclides by benthic biota may occur by direct sediment ingestion (11). In tissues of various invertebrate infauna concentrations of plutonium of 5 to 10 times those in the sediment have been found.These findings suggest that sediment-associated transuranics are available to biota (12). In laboratory experiments with polychaetes more than 90 percent of the plutonium were derived from a source other than sediment, possibly from deposited material or interstitial pore water (11). Thus, the sediment pathway is responsible for only a few percents of the total body burden of plutonium in polychaetes (13). Considering the high concentration factors in biota of 100 to 1000 reported in the literature for direct uptake from water one may conclude that water, possibly interstitial water, is the predominant pathway for uptake of transuranics by sediment infauna.

The processes involved in the transfer of radionuclides from sediments to benthic infaunal organisms are still unclear and may depent on the physico-chemical forms of the different isotopes present in the sediment and interstitial water.

The transfer factors for contaminated sediments and whole bodies of infaunal organisms that ingest sediment particles continously were found to be very low for plutonium, americium and technetium.The values obtained range from 0.1 to 0.001 for polychaetes, molluscs, and crustaceans(11,14, 15),resulting in a relatively small net uptake of those radionuclides from contaminated sediments. In this process part of the radionuclides transferred to infaunal species will come from the sediment's interstitial pore water while another part would be obtained by direct transfer from sedimentary particles to the organisms (14).

In conclusion, the literature data and experimental results show a potential remobilisation of transuranic elements from biodisturbed sediment layers by benthic infaunal species. However, the relatively high concentration factors of 1000 determined for the uptake from water and the very low transfer factors of 0.001 for sediments indicate that interstitial or pore water and not the sediment particles will be the predominant source of transuranics for benthic infaunal organisms.

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BIOGEOCHEMICAL STUDIES OF LONG-LIVED RADIONUCLIDES IN MARINE ENVIRONMENTS

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In Enewetak and Bikini lagoons, $^{239,240}Pu$ is always present at levels higher than for fallout, in water samples, indicating remobilisation from sediments. The respective water levels are 21 fCi l^{-1} and 42 fCi l^{-1}, and lagoon inventories 0.96 and 1.2 Ci, which are 0.08% of sediment inventories. Small amounts of ^{241}Am also solubilise. Pu attached to suspended particles is mostly $Pu^{III,IV}$, and if soluble is $Pu^{V,VI}$. Concentrations of ^{90}Sr, ^{137}Cs, $^{239,240}Pu$, ^{241}Am, ^{207}Bi and ^{210}Pb. ^{210}Bi and ^{210}Po in fish showed some variation with trophic level. Values increased between levels 2 and 5 for ^{90}Sr, $^{239,240}Pu$, ^{241}Am, but not ^{137}Cs. Concentration factors varied, and a single generic value for all fish species was not possible. Extrapolation of results from contaminated lagoons to lesser contaminated lagoons was not possible because in the former radionuclides were fused with $CaCO_3$ and dissolve in the gut of fish to some extent. Speciation is different in lesser contaminated lagoons. 80% of ^{207}Bi was in the muscle of goat-fish but less than 1% for surgeonfish and mullet. Evidence was obtained that the isotope is translocating. Similarly ^{210}Bi formed in fish bone translocates to liver. In the North-east Atlantic dumpsite, only global fallout levels were found for radionuclides which could have potentially leached from the wastes.

1. Introduction

Many of the questions regarding deep-sea disposal of transuranium elements and other long-lived radionuclides can be partially answered from studies at contaminated, more accessible locations -- here some of the processes, reactions, and rates that influence the fate of these radionuclides in the marine environment can be identified and evaluated. Reliable information on the environmental behavior of these radionuclides in the ocean is required to improve our understanding of the pathways that may lead back to man from any future practices involving disposal either onto or into marine sediments.

For several years, we have conducted studies related to the cycling of long-lived radionuclides at several locations in the Pacific which include the Farallon Islands waste disposal site off the coast of California, USA; Marshall Islands with the emphasis on Bikini and Enewetak Atolls; the previous United States proving grounds in the Pacific; Johnston Atoll; and San Clemente Island off the coast of

California, USA. In addition to the Pacific studies, a deep-sea program was recently initiated in the vicinity of the Northeast Atlantic radioactive waste-disposal site. Many of the sites mentioned in the Pacific are among the few in the world where long-lived radionuclides, now found in solution or accumulated by organisms, originate from bottom sedimentary deposits. Therefore, research results obtained from these areas have relevance in assessing the use of the sea bottom for radioactive waste disposal. Results from a few studies, conducted during the tenure of this research agreement and which are relevant to seabed disposal of radioactive wastes, are briefly discussed in this report.

2. Mobilization of Plutonium from Enewetak and Bikini Lagoon Sediments to Seawater.

One important question related to the long-term behavior of the transuranium elements in the marine environment is whether the radionuclides, after deposition in bottom sediments, can return to the water column and eventually re-enter biological food chains remote from the point of origin. At some sites, contaminated by global fallout or surface discharges, where high concentrations are maintained in the overlying water column, mobilization of plutonium from sedimentary sources to solution is difficult to demonstrate(1). However, at sites where plutonium was introduced directly onto sedimentary materials or where current inputs to sediments are small, mobilization of plutonium can be easily identified(2-7). For example, the lagoon sediments at Bikini and Enewetak, the sites previously known as the Pacific Proving Grounds, were contaminated with fission and activation products from nuclear devices tested there by the United States between 1946 and 1958. Following the last nuclear test at Enewetak in 1958, the residual radionuclides deposited to the lagoon water either settled rapidly to the bottom sediments or remained as dissolved or particulate species in the water and were eventually discharged to the ocean. If we accept the thesis of no mobilization, we would observe a concentration of dissolved plutonium (and americium) in the lagoon water mass during any time subsequent to 1958 at a level equivalent to that from global fallout in the north equatorial Pacific surface water, the replacement water for the lagoon. Table 1 shows the variation of the mean $^{239+240}$Pu activity in filtered samples of seawater collected during the years indicated from different locations in the lagoons at Enewetak and Bikini. Fallout levels of $^{239+240}$Pu in the surface waters of the north equatorial Pacific have averaged 0.4±0.2 fCi/l over the last 10 y(5).

Concentrations of $^{239+240}$Pu greater than fallout background concentrations are found in the water sampled from all locations throughout the lagoons. This is a direct indication that $^{239+240}$Pu has been continuously mobilized over the years to solution from the solid phases in these environments. The variations between the average soluble concentrations of $^{239+240}$Pu determined from samples obtained during the periods indicated are not, at this time, considered significant and the assumption is made that the standing average amount of plutonium in the lagoon water mass at any time, is constant. Stated differently, steady state conditions have been established for $^{239+240}$Pu partitioning from the sedimentary reservoirs at these atolls to solution. Since 1972 the average "soluble" $^{239+240}$Pu at Enewetak has been 21 fCi/l. At Bikini the mean value from 1972 to 1982 has been 42 fCi/l. With the appropriate dimensions for each lagoon, these concentrations convert to lagoon inventories of 0.96 and 1.2 Ci at Enewetak and Bikini, respectively. Particulate concentrations are not included in these estimates. These quantities represent 0.08% of the sediment inventories determined to a depth of 16 cm at each atoll. The mean quantity of $^{239+240}$Pu mobilized and found in solution at any time represents a small fraction of the inventory associated with the major reservoir at the atolls. Mobilization of $^{239+240}$Pu from marine deposits is a slow, but nevertheless real process.

Small amounts of ^{241}Am are also capable of dissociating from these marine deposits. ^{241}Am is more firmly bound to the sediments than $^{239+240}$Pu. The amount of $^{239+240}$Pu mobilized to solution at the atolls can be reasonably predicted using a K_d of approximately 2.3×10^5 and the mean sediment concentrations.

The mobilized $^{239+240}$Pu at Enewetak and Bikini has solute-like characteristics and different valence states coexist in solution. The largest fraction of the soluble plutonium is in an oxidized form (+V or VI). Quantities associated with suspended particulate material and sediments are predominately in the reduced state (+III or IV). The sorption-desorption process is not completely reversible because of changes that occur in the relative amounts of the mixed oxidation states in solution with time. The oxidized forms of $^{239+240}$Pu in solution have a lesser tendency to associate with sedimentary or particulate material than reduced plutonium. Complexation after mobilization also affects the resorption rate. Therefore, any characteristics of $^{239+240}$Pu described at a point of reference may not necessarily be relevant to explain behavior after mobilization and migration in solution. Some small fraction of any $^{239+240}$Pu placed on the surface of the sea floor in oxygenated environments should, in time, disperse to the overlying water mass and migrate from its original site. The ^{241}Am should remain more firmly fixed to the sedimentary material near the point of introduction. The rate of disappearance of the two radionuclides from marine deposits will depend on the physical, biological, and chemical characteristics of the sediments and the rate of water movement into and out of the contaminated region.

Table 1. The $^{239+240}$ Pu Average Lagoon Water Concentrations. [a]

Enewetak Lagoon

933 km^2--Lagoon Area
49 m--Average Depth

Month and Year and Number of Water Samples in Parenthesis

	10-12/72 (35)	7/74 (71)	5/76 (29)	5/82 (23)
Soluble (fCi/liter)	22	25	16	17
Particulate (fCi/liter)	10	19	13	nd
TOTAL	32	44	29	

Bikini Lagoon

629 km^2--Lagoon Area
45 m--Average Depth

Month and Year and Number of Water Samples in Parenthesis

	12/72 (17)	1-2/77 (26)	9/82 (21)
Soluble (fCi/liter)	42	49	34
Particulate (fCi/liter)	13	nd	nd
TOTAL	55		

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[a] Arithmetic mean values.
nd not determined

3. Concentrations of ^{90}Sr, ^{137}Cs, $^{239+240}$Pu, ^{241}Am, ^{207}Bi and ^{210}Pb-^{210}Bi-^{210}Po in fish from the Marshall Islands.

Studies of the accumulation of long-lived radionuclides by marine organisms and specifically by fish eaten by man, have been conducted in different Marshall Island Atolls where sediments play a role in determining body burdens of radionuclides in some fish.

Concentrations of ^{90}Sr, ^{137}Cs, $^{239+240}$Pu, and ^{241}Am were determined in tissues of fish, near-shore surface sediments, and seawater from several atolls contaminated with close-in fallout debris generated at the Pacific Proving Grounds in the late 1940s through the late 1950's. The atolls were sorted with respect to present contamination levels detected in the surface sediments from the lagoons. The "A" group of atolls, which include Ailuk, Likiep, Taka, Ujelang, Uterik and Wotho, have the lowest mean level of contamination and Rongelap has the highest. The "B" group of atolls consists of Ailinginae, Bikar and Rongerik which have higher levels of contamination in the surface sediments than the "A" group but less than at Rongelap. Sediment-to-lagoon water concentration ratios for these radionuclides (a measure of the sediment/ water distribution coefficient) increased proceeding from the lesser contaminated atolls to Rongelap. Fractions of the radionuclides still detected in the marine environment are irreversibly bound with the mineral matrix of the sediments, and equilibrium conditions do not exist at all atolls. Mean radionuclide concentration factors were computed for bone and muscle of the fish representing trophic levels II-V from the groups of atolls by relating the measured tissue concentrations to those in filtered lagoon seawater. Values of ^{90}Sr concentration factors for bone and muscle of fish decrease between the 2nd and 5th trophic level. The concentration factor for bone of bottom feeding fish is the largest at atolls where ^{90}Sr is more permanently fixed to the near shore sedimentary material. There was no unique relationship between trophic levels of the fish and the ^{137}Cs muscle concentration factor. Some of the variability in the ^{137}Cs concentration factors is best related to differences in diet, with concentration factors being lower for bottom feeding fish than for pelagic species. Higher concentration factors are also found for ^{137}Cs at atolls where the radionuclide is still detected in bottom sediments.

Values of $^{239+240}$Pu and ^{241}Am concentration factors for bone followed the same trend noted for ^{90}Sr, decreasing between II and V trophic level. Ratios of ^{241}Am to $^{239+240}$Pu increased in bone and muscle between 2nd and 5th trophic level species. ^{241}Am seems to be more biologically available than $^{239+240}$Pu to higher trophic level species from the lagoons, whereas at lower trophic levels the opposite seems to be the case. Both $^{239+240}$Pu and ^{241}Am concentration factors are greater for bottom feeding species from the more contaminated atolls than found for the same species at the lesser contaminated atolls. This feature is common for all the long-lived man-made radionuclides determined in this study. The following is a partial ranking of the radionuclide concentration factors in muscle for some species from the different atolls.

Surgeonfish muscle concentration factors (Trophic Level II)
A atolls ^{137}Cs $\geq$ $^{239+240}$Pu > ^{241}Am > ^{90}Sr

B atolls ^{137}Cs $\geq$ $^{239+240}$Pu > ^{241}Am > ^{90}Sr

Rongelap $^{239+240}$Pu > ^{137}Cs > ^{241}Am > ^{90}Sr

Mullet muscle concentration factors (Trophic Level II)
A atolls $^{239+240}Pu > ^{137}Cs > ^{241}Am > ^{90}Sr$
Goatfish muscle concentration (Trophic Level III)
A atolls $^{137}Cs \geq ^{239+240}Pu > ^{241}Am > ^{90}Sr$
Trophic V species
All atolls $^{137}Cs > ^{239+240}Pu > ^{241}Am > ^{90}Sr$

This ranking shows there is no precise ordering of the values of concentration factors for all fish, which negates the use of a single generic value for all fish species. The ordering is altered by species, trophic level, and degree of bottom sediment contaminations.

Bottom-feeding fish have the ability to extract radionuclides that are irreversibly bound to sedimentary deposits and attain tissue burdens that are larger than the concentrations found in the same species from environments where near-equilibrium conditions have been established. The values for the concentration factors generated at the lesser contaminated atolls cannot be used with water concentrations to generate reliable estimates of concentrations in tissues of species from the more contaminated lagoons. An explanation for this anomaly is that some bottom-or coral-feeding fish with diets containing, in part, carbonate material have the ability to lower their gut pH during feeding, which results in dissolution within the gut of a fraction of the calcium carbonate ingested with food. Fractions of the ^{137}Cs, ^{90}Sr, $^{239+240}Pu$, and ^{241}Am previously fixed or fused within the calcium carbonate matrix during the period of nuclear testing at Enewetak and Bikini are released by the digestive juices and can pass across the gut wall of the fish.

Contaminants irreversibly fixed to carbonate sediments are not isolated from biological cycles in the ocean. Higher trophic level species that do not rely on sediments or coral for this source of food show no such increasing trend in the values for the concentration factors between differently contaminated atolls.

Another study conducted at Enewetak and Bikini Atolls involved the determination of ^{207}Bi and natural ^{210}Pb-^{210}Bi-^{210}Po in tissues of different fish. ^{207}Bi was produced during the series of nuclear tests conducted by the United States at Bikini and Enewetak Atolls between 1946 and 1958, possibly by reactions such as ^{207}Pb (p,n) or ^{206}Pb (p,γ), assuming stable lead was present during testing as shielding material near the nuclear devices(8). Table 2 shows concentrations of ^{207}Bi determined by gamma spectrometry in tissues and organs of several species of fish collected from Bikini and Enewetak during different years.

Most striking is the range of concentrations in tissues and organs among different species of fish collected simultaneously from the same location. Highest concentrations of ^{207}Bi were consistently detected in the muscle and other tissues of goatfish and some of the pelagic lagoon fish compared to those of other reef fish such as mullet, surgeonfish, and parrotfish. Over 80% of the whole-body activity of ^{207}Bi in goatfish is associated with the muscle tissue, whereas less than 1% is found in the muscle of surgeonfish and mullet. The concentration factor for ^{207}Bi is not single-valued for fish and varies with the species.

Concentrations of ^{210}Po were also determined in the muscle of a few goatfish, mullet and surgeonfish from Bikini Atoll. The average concentration in goatfish flesh (0.67 pCi/wet g) exceeded the level in surgeonfish (0.065 pCi/wet g) and mullet (0.38 pCi/wet g). These data coupled with the observation of higher levels of ^{207}Bi in goatfish, led us to speculate that similar enrichment might be expected for ^{210}Bi ($t_{1/2}$ = 5.01 d), the precursor of ^{210}Po and direct daughter product from decay of ^{210}Pb. Any unsupported ^{210}Bi detected could be a potential source for some fraction of excess ^{210}Po detected in marine organisms. A variety of fish representative of different trophic levels were caught at Bikini, Enewetak, Rongelap, and Kwajalein Atolls for the analysis of ^{210}Bi, ^{210}Po, and ^{210}Pb. Separations of these radionuclides were made onboard the research vessel within 24 h of collection to minimize the unavoidable growth-decay corrections.

The ^{210}Bi concentrations in liver and flesh from all species exceed those of its percursor ^{210}Pb measured in these tissues. Therefore, some account of excess ^{210}Bi in edible portions of freshly caught and rapidly consumed fish should be made in radiological dose estimates from natural radionuclides in marine food pathways. Based on the ^{207}Bi results and the assumption that any unsupported ^{210}Bi accumulated by fish from food or water would relate to ^{207}Bi concentrations, we anticipated levels of ^{210}Bi in the muscle of goatfish several orders of magnitude larger than the unsupported concentrations in surgeonfish, mullet, and parrotfish. Rather, we found no significant differences in concentrations of ^{210}Bi in the muscle among all the species. It is clear, therefore, that the excess of ^{210}Bi in the muscle and liver of surgeonfish, mullet, and parrotfish is not from its percursor in the tissue nor from the environmental sources from which ^{207}Bi is derived. The data suggests that the excess ^{210}Bi may be translocated to muscle and liver tissue following the decay of ^{210}Pb accumulated in the bone. All unsupported ^{210}Po measured in fish, and possibly in other organisms, does not necessarily have to result directly from the food chain. Some fraction, which may vary with the species, of unsupported ^{210}Po in specific tissues such as muscle and liver may result from redistribution and decay of ^{210}Bi generated from ^{210}Pb accumulated in bone.

Concentration factors for ^{210}Po in muscle to that in filtered seawater have been calculated using a mean value of 31±3 fCi/l for ^{210}Po measured in 12 lagoon and ocean surface-water samples. Values range from 8×10^2 for surgeonfish muscle to 2.3×10^4 for goatfish.

4. Plutonium in Northeast Atlantic Sediments

Deep-sea disposal of packaged, low-level radioactive wastes has occurred at several sites in the Northeast Atlantic. However, since 1977, disposal has been restricted to a single site, 4×10^3 km^2 in area, within 10 mi north and south of 46°N and between 16°W and 17°30'W. A program of coordinated scientific studies was initiated in 1980 by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development to develop a site-specific model for predicting radiation exposures from the disposed wastes. Task groups on physical oceanography-geochemistry, biology, modeling, and radiological surveillance were established to provide scientific input on the physical, geochemical, and biological processes controlling the behavior of radionuclides in the deep ocean and specifically at the disposal site. As part of this effort, various cooperative studies were undertaken with other investigators to improve our understanding of the behavior of long-lived radionuclides in pelagic sediments.

The concentrations and inventories of $^{239+240}$Pu in sediments from within the boundaries of the low-level radioactive waste-disposal site in the Northeast Atlantic are no different from global fallout levels in deep-sea sediments from this region of the Atlantic. No man-made gamma-emitting radionuclides were above detection limits in the sediment samples analyzed. There is no indication that past disposal practices have led to an area-wide contamination of the site with waste-related radionuclides. The $^{239+240}$Pu sediment-depth distributions indicate

Table 2. Concentrations of ^{207}Bi in fish from Enewetak and Bikini Atolls

Atoll and island*	Year	Common name**	^{207}Bi (pCi/kg wet)† Muscle	Bone	Viscera	Stomach content	Skin	Liver
E-24	80	Mullet (Crenimugil)(II)	1.1 (27)	<2	578 (1)	1490 (2)	<1	30 (20)
		Surgeonfish (II)	1.8 (29)	5 (30)	91 (2)	--	4.5 (20)	391 (2)
		Goatfish (II)	656 (1)	283 (2)	661 (1)	--	465 (2)	1190 (1)
		Snapper (Lethrinus)(V)	263 (2)	102 (4)	713 (2)	92 (4)	266 (3)	--
		Snapper (Lutjanus)(V)	191 (2)	198 (2)	1130 (2)	--	150 (2)	--
		Bonito (V)	106 (3)	60 (24)	421 (3)	124 (12)	90 (18)	662 (7)
E-10	78	Mullet (Crenimugil)(II)	<2	<5	1150 (1)	1420 (2)	<2	<11
		Surgeonfish (II)	<1	<6	20 (18)	65 (16)	<8	89 (10)
		Goatfish (III)	6530 (2)	1770 (11)	9560 (1)	1220 (7)	4570 (1)	7460 (2)
		Parrotfish (IV)	<2	<10	<12	--	<4	--
B-5	81	Mullet (Crenimugil)(II)	<2	<14	44 (9)	-	<10	<40
		Surgeonfish (II)	<4	<11	21 (35)	<40	<14	36 (24)
		Goatfish (III)	56 (4)	22 (3)	145 (12)	242 (18)	37 (25)	50 (10)
		Parrotfish (IV)	<4	<14	<49	51 (23)	<23	<50
B-1	78	Mullet (Crenimugil)(II)	4 (20)	<4	54 (11)	124 (11)	<3	116 (15)
		Mullet (Neomyxus)(II)	<1	<8	68 (6)	100 (26)	<4	48 (25)
		Surgeonfish (II)	<2	<25	49 (20)	<190	<30	<100
		Goatfish (III)	1360 (2)	400 (4)	206 (2)	1070 (11)	960 (2)	3020 (2)
		Jack (IV)	121 (2)	19 (35)	120 (11)	<60	--	190 (20)

* E = Enewetak Atoll and B = Bikini Atoll. Numbers designate islands.

† The 1 σ counting error expressed as the percentage of the listed value appears in parenthesis. 1 pCi = 37 mBq.

** Trophic level shown in parenthesis

that downward transport of labelled surface material has occurred to depths greater than 15 cm in the sediment column. There are well-defined maxima in the majority of the $^{239+240}$Pu profiles. This feature is not consistent with one-dimensional vertical mixing models. Heterogenous bioturbation is the dominant mechanism moving $^{239+240}$Pu from the sediment surface downward and laterally in Northeast Atlantic pelagic sediments.

5. Quality-Assurance and Intercomparison Program

During the last 12 years we have participated in a large number of national and international intercalibration exercises and have conducted a continuing rigorous internal quality assurance program. In the GEOSECS program we provided quality control data of many kinds for the measurements of radionuclides in seawater. These results are discussed in greater detail elsewhere(9). Some additional quality-control data were generated during the northern Marshall Island survey and have been discussed(10). More recently, the sediments from the Northeast Atlantic were processed for the radiochemical separation of plutonium radionuclides and ^{241}Am using modifications of published techniques that were tested on an IAEA intercalibration exercise performed in conjunction with the sample analysis. The results submitted for $^{239+240}$Pu and ^{241}Am concentrations in sediment sample SD-N-1/1, distributed by the Monaco Laboratory of the IAEA, are shown in Table 3 along with the median values chosen as the most reliable estimators of the true values(11). Agreement between our reported values and the most reliable estimators of the true value may be considered satisfactory. The mean $^{239+240}Pu$ concentration of the "standard" sediment is comparable to the mean concentration in surface-sediment increments from within and outside the dump site.

We currently are conducting other intercalibration exercises with Portugal (deep sea fish); IAEA (seaweed and sediment); UK (sediment); and other LLNL divisions. We maintain a large number of National Bureau of Standard samples and IAEA standards that are continually used on our analytical program to validate detector calibration and separation procedures.

Table 3. Results of intercomparison of artificial radionuclide measurements on marine sediment sample SD-N-1/1.

Radionuclide	LLNL mean[a] $fCig^{-1}$	LLNL mean[a] $mBqg^{-1}$	Most reliable estimator of true value $mBqg^{-1}$
^{238}Pu	5.1±0.8	0.19±0.03 (21)	0.18
$^{239+240}Pu$	15.2±1.1	0.56±0.04 (21)	0.56
^{241}Am	13.0±1.6	0.48±0.06 (11)	0.49
^{60}Co		10.9±0.5 (3)	11.8
^{137}Cs		15.2±0.8 (3)	14.0

[a] Number of samples analyzed shown in parentheses.

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Acknowledgment

The work in the Pacific was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48 and the work in the Northeast Atlantic was supported by the Office of Radiation Programs, United States Environmental Protection Agency (DOE-EPA Interagency Agreement AO89F00070).

INTERCOMPARISON STUDIES OF TRANSURANICS IN NORTH ATLANTIC DEEP SEA SEDIMENTS FROM THE NEA DUMPSITE

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Abstract

Detailed intercomparison of two cores from the dumpsite showed that horizontal activity distribution was not homogeneous for ^{239,240}Pu. However the vertical inventory remains the same. There was no systematic bias between the Pu analysis by the two laboratories. The ^{238}Pu/^{239,240}Pu mean ratio was 0.08±0.02 and for ^{241}Am/^{239,240}Pu was 0.26±0.12, both compatible with global fallout.

1. THE SAMPLES

Two cores (Nos 4 and 11) taken on the Tyro 82 cruise to the NEA dumpsite (45°50'N to 46°10'N and between 16°W and 17°30'W)in August-September 1982 [1] were obtained from Dr. V. Noshkin, Lawrence Livermore National Laboratory. The cores had been sectioned into 1 cm depth increments and the surface area of each section is 28.2 cm^2. The two cores were subcores from two different 0.25 m^2 Mark III boxcores, from each of which Dr. Noshkin had analysed another duplicate subcore.

2. RESULTS

Ten (or twenty for the weakest samples) grammes aliquots of dried sediments were analysed for Pu and Am by the methods of Talvitie [2] and Holm [3].

Core 4 (Table 1) shows an exponentially decreasing ^{239,240}Pu concentration with a half depth of 2 cm. Core 11 (Table 2) shows a subsurface maximum at 2-4 cm depth. The ^{239,240}Pu inventories of the two cores down to 11 cm were 5.83 Bq m^{-2} (0.16 mCi km^{-2}) and 7.01 Bq m^{-2} (0.19 mCi km^{-2}), respectively. Noshkin [1] found 0.16 and 0.22 mCi ^{239,240}Pu km^{-2}, respectively in his corresponding subcores. The mean ratio of the concentrations

Table 1. Plutonium and americium in core T 8204 B collected at the NEA dumpsite in 1982

No.	Segment in cm	$^{239,240}Pu$		^{239}Pu	^{241}Am
		Bq kg^{-1}	Bq m^{-2}	Bq kg^{-1}	Bq kg^{-1}
PMSG 088	0-1	0.36 (7)	2.43	0.023 (23)	0.093(10)
- 89	1-2	0.164 (10)	1.17	0.0156(30)	0.018(32)
- 90	2-3	0.100 (10)	0.71	0.0084(27)	-
- 91	3-4	0.067 (13)	0.50	0.0047(33)	-
- 92	4-5	0.049 (16)	0.34	-	-
- 93	5-6	lost	-	-	-
- 94	6-7	0.0148(18)	0.11	-	-
- 95	7-8	0.040 (17)	0.30	-	-
- 96	8-9	0.0182(21)	0.14	-	-
- 97	9-10	0.0092(27)	0.07	-	-
- 98	10-11	0.0067(33)	0.06	-	-

The relative SD (in %) due to counting statistics are shown in brackets.

Table 2. Plutonium and americium in core T 8211 B collected at the NEA dumpsite in 1982

No.	Segment in cm	$^{239,240}Pu$		^{239}Pu	^{241}Am
		Bq kg^{-1}	Bq m^{-2}	Bq kg^{-1}	Bq kg^{-1}
PMSG 198	0-1	0.23 (9)	1.41	0.0172(32)	0.098(12)
- 199	1-2	0.093 (11)	0.66	-	-
- 200	2-3	0.172 (6)	1.22	0.0187(30)	0.054(14)
- 201	3-4	0.207 (7)	1.63	-	0.038(18)
- 202	4-5	0.054 (17)	0.40	-	-
- 203	5-6	0.074 (10)	0.55	0.0040(33)	-
- 204	6-7	0.027 (16)	0.21	-	-
- 205	7-8	0.030 (17)	0.22	-	-
- 206	8-9	0.035 (17)	0.28	-	-
- 207	9-10	0.045 (14)	0.33	-	-
- 208	10-11	0.0135(27)	0.10	-	-

The relative SD (in %) due to counting statistics are shown in brackets.

in the various layers found by Risø and Livermore was 1.08 ± 0.70 (N=18; ± 1SD). This shows that the horizontal activity distribution of the boxcores are inhomogeneous. However, the inventories of the 0-11 cm layers within a core are the same. The results, furthermore, show that there is no systematic bias between the Pu-analysis performed by Livermore and Risø.

The $^{238}Pu/^{239,240}Pu$ mean ratio was 0.08 ± 0.02 (N=7; ± 1SD) and the $^{241}Am/^{239,240}Pu$ mean ratio was 0.26 ± 0.12 (N=5; ± 1SD). These ratios are compatible with those expected from global fallout. We can thus support the conclusion of Noshkin [1] who stated that no evidence of plutonium contamination in these samples from any other source than global fallout had been found.

3. INTERCALIBRATION

Throughout the years Risø National Laboratory has participated in the intercalibration exercises organised by the IAEA Monaco Laboratory.

In the intercomparison of marine sediment SD-N-1/1 [4] we had laboratory code No. 3. The mean of the accepted $^{239,240}Pu$ results was 0.57, we found 0.53 (mBq g^{-1}); our ^{238}Pu and ^{241}Am results were also within the accepted range.

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TECHNETIUM DISTRIBUTION AND ACCUMULATION IN MARINE SEDIMENTS AND BIOTA*

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Abstract

Technetium normally exists in marine environments as pertechnetate Tc^{VII}. However when sediments are reduced and organic rich, it becomes fixed rapidly to them. Bacterial activity does not seem to be responsible. Concentration factors for Tc in biota are generally 10-20 but two exceptions are macrophytic algae (1100) and polychaetes (300-800). Biological half lives are weeks or months. Retention was generally about 20% of that in the food source, and 25% of that was retained in the digestive gland or liver.

In the last years the principle objectives of radioecological studies at this laboratory have been to gather information on and further understanding of the environmental behaviour of long-lived radionuclides with special respect to technetium. The only recent introduction of technetium, an artificial radioelement which has no stable isotopes, into the environment has been of considerable concern regarding the cycling of its long-lived radioisotope Tc-99 in the geo- and biosphere (1). As other long-lived radionuclides,such as transuranics, technetium is found in the three major compartments of the marine environment,i.e. in solution, in biota, and in sediments. During the period covered by this report considerable effort has been expended on studying the behaviour of technetium in these compartments under laboratory conditions.

In aqueous solutions technetium may occur in various physico-chemical forms according to thermodynamic considerations, but in the ranges of pH and Eh values normally occurring in the marine environment pertechnetate (VII) is clearly the most stable chemical form (2),which has been confirmed also experimentally. It has been shown that about 90% of hydrazine-reduced technetium (IV) is rapidly reoxidized in well oxigenated sea water to pertechnetate within less than one hour, while the remaining 10% being oxidized slowly. Hence, in all further laboratory studies only pertechnetate was used in order to ensure constant physico-chemical behaviour of the radioisotope during the experiments.

A considerable effort has been expended in order to identify the mechanisms by which technetium becomes incorporated into sediments(3).

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* Contribution N° 2196 of the CEC Radioprotection Programme.

In investigations using reducing sediments rich in organic carbon rapid disappearance of pertechnetate from the water column has been observed. The fixation rate of technetium in the sediment was found to be dependend on several factors such as physico-chemical characteristics of the sediment bed, mass ratio between sediment and water,area of the sediment/water interface etc. Investigations on the role of bacterial activity in the fixation process of technetium within sediments revealed only an indirect action of bacteria in that they contribute in determining chemical and physical characteristics of the sediment column. Therefore, the principle factors responsible for the immobilization of technetium in sediments are most likely redox conditions while diffusion to deeper, anoxic layers in the sediment is most probably the limiting factor in the fixation process of technetium.

Studies on the biological availability of technetium to marine organisms were aimed at assessing and eventually better controlling the impact of technetium releases on man and the environment. In laboratory experiments concentration factors, biological half-lives as well as assimilation capacities of a variety of marine organisms, including algae, invertebrates and fish have been determined (4). Generally concentration factors were found to be quite low (10 - 20) with some exceptions like macrophytic brown algae (Fucus; CF 1100) and polychaetes (CF 300-800). Rates of loss after accumulation of technetium from water or contaminated food were high resulting in relative short biological half-lives of some weeks or months (5,6). Retention of technetium in marine organisms was low and amounted about 20% of the radioactivity present in the food stuff, of which about 25% was retained in the digestive gland or liver.

Despite the considerable amount of information recently gathered on the environmental behaviour of technetium there are still requirements for further studies in order to sufficiently assess the biogeochemical cycling and potential impact of technetium on man and the environment.

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MEASUREMENT OF LONG-LIVED RADIONUCLIDES IN THE ATLANTIC RELATED TO RADIOACTIVE WASTES DEEP-SEA DISPOSAL*

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Abstract

Deepsea fish, possibly potential links in a food chain to main from the N.E.Atlantic dump-site were analysed for ^{137}Cs, ^{210}Po, ^{238,239,240}Pu. ^{137}Cs is lower in such fish than most other fish tissues. This was truealso for ^{210}Po. Sediments from the site gave similar results to those reported by other authors. Unfiltered water samples were analysed for ^{239,240}Pu and results were (in mBq m^{-3}) 12 for the Tagus estuary, 26 for 1500 m sample off Madeira, and 30 for one 3800 m sample NW of Portugal.

1. INTRODUCTION

The black scabbard (*Aphanopus carbo*) fishery is the only deep sea one known in the north-eastern Atlantic, representing a potential pathway back to man for long-lived dumped radionuclides. So, a study of this fishery was implemented, including landing statistics, distribution, trophic relationships and radionuclide concentrations.

Along this study, fishes from several species also caught at different depths near Madeira island and south of Lisbon, were identified and analysed. Two shallow water fish species were selected for comparing their radionuclide concentrations, the barracuda (*Sphyraena sphyraena*) and the scabbard (*Lepidopus caudatus*).

Fish, sea water and sediment samples were analysed for their contents in transuranics. ^{137}Cs and ^{210}Po were also analysed in fish muscle.

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* Research Contract 3091/RB.

2. METHODS

Fish muscle was prepared for analysis by drying and incinerating; isotopic tracers were added. The ashes were analysed by direct gamma spectrometry for determining ^{137}Cs. For plutonium and americium radiochemical separation, samples were spiked with ^{236}Pu, ^{243}Am and ^{244}Cm. Transuranic analysis involve ion exchange chromatography (AG 1x8), solvent extraction with HDEHP and electroplating. The transuranic elements were measured by alpha spectrometry, using silicon barrier surface detectors.

Some of the fish were dissected and the different organs were analysed for their content in ^{210}Po by spontaneous plating from HCl-$HClO_4$ solutions on silver disks followed by alpha spectrometry.

3. RESULTS

3.1. Black scabbard fishery

Fish landing statistics obtained at Madeira, for the last ten years, confirm the economic and social importance of black scabbard fishery for the region.

Some fishing cruises to south of Madeira (with sampling at different depths) have been effected. They enable us to conclude that scabbard lives mainly between 800 and 1400 m; besides, it has never been caught near the bottom.

Having never got young specimens, we can admit the possibility of vertical migrations for this species.

Other ones were fished, identified and analysed as well.

3.2. Transuranics

^{238}Pu results were always below detection limit. So, Table 1 only presents $^{239+240}Pu$ concentrations in fish muscle for some of the analysed samples. In black scabbard muscle they are about 0.1 mBq/kg fresh. In other species, either from shallow waters or from the deep slope, higher values, around 1 mBq/kg, were found. Black scabbard values were confirmed through an analysis performed by V. Noshkin at LLNL. Furthermore, the quality of our data in plutonium determinations is confirmed by the results obtained in the intercalibration exercises organized by ILMR, Monaco.

They can also be compared with those reported by Noshkin (1), Triulzi et al (2) and Bowen (3).

TABLE 1: $^{239+240}$Pu in Fish muscle[a]

REFERENCE[b]	SCIENTIFIC NAME	DEPTH (m)	mBq/kg fresh	fCi/g dry
1979 M	Aphanopus carbo	1200	0.12±0.06	0.017±0.009
1980 M	Aphanopus carbo	1200	0.13±0.08	0.019±0.011
1982 M	Aphanopus carbo	1200	<0.3	<0.04
1983 M	Aphanopus carbo[c]	1200	0.1(35%)	0.02(35%)
1980 P	Malacocephalus laevis	600	1.0±0.5	0.13±0.07
1980 P	Beryx decadactylus	400	0.8±0.5	0.10±0.06
1980 P	Deania calceus	1000	<1	<0.2
1982 M	Helicolenus dactylopterus	600	1.2±0.2	0.17±0.03
1981 M	Sphyraena sphyraena	shal	1.0±0.3	0.12±0.03
1983 P	Lepidopus caudatus	200	1.1±0.4	0.14±0.05

[a] Lower detection limit at 95% confidence level; error 1 sigma propagated

[b] M: Madeira; P: west coast of Portugal

[c] Analysed by V. Noshkin, LLNL

In some predatory fish, like tuna and squalidae, higher concentrations (3-4 mBq/kg fresh) were obtained, but they need further confirmation.

Unfiltered water samples were also analysed for their plutonium content. $^{239+240}$Pu concentrations found were 12 mBq/m^3 for an estuarine water (Tagus river), 26 for a 1500 m depth water collected off Madeira island and 30 mBq/m^3 for one 3800 m depth sample from the north -west coast of Portugal. The statistic errors for these determinations being about 10%. These results can be compared with those reported by Miettinen et al (4), Kautsky & Eicke (5), Holm & Persson (6), Livingstone et al (7) and Ballestra et al (8), among many others.

Such values lead to a concentration factor of about 5 for the black scabbard fish. For other species it would range from 40 to 80. However few results are yet available from the areas where these were caught.

Some sediment samples, from the deep sea, were also analysed for plutonium, as well as for ^{137}Cs and ^{226}Ra by gamma spetrometry. The results correspond to a homogenized 10 cm surface layer. Results for plutonium (see Table 2) are within the range of values reported by Noshkin, for the northeast Atlantic (9), and can also be compared to those reported by Triulzi et al (2) and Ballestra et al (8).

TABLE 2: ^{238}Pu, $^{239+240}$Pu, ^{226}Ra and ^{137}Cs in deep-sea sediments[a]

YEAR	DEPTH (m)	COORDINATES	^{238}Pu (µBq/g)	$^{239+240}$Pu (mBq/g)[c]	^{226}Ra (Bq/g)[c]	^{137}Cs (mBq/g)[b]
1980	1790	39°32' N 09°47' W	<3[b]	0.18±0.02	0.13±0.02	<4
1981	4200	39°35' N 10°20' W	<4[b]	0.04±0.02	0.11±0.02	<4
1982	1465	32°35' N 17°05' W	9±3[c]	0.27±0.02	0.06±0.04	<2

[a] On dry weight basis

[b] Lower detection limit at 95% confidence level

[c] Errors given are 1σ

TABLE 3: ^{137}Cs in fish muscle

REF.[a]	SCIENTIFIC NAME	DEPTH (m)	Bq/kg fresh
1979 M	Aphanopus carbo	1200	0.25±0.04
1979 M	Aphanopus carbo	"	0.38±0.07
1979 M	Aphanopus carbo	"	0.40±0.07
1980 M	Aphanopus carbo	"	0.47±0.07
1982 M	Aphanopus carbo	"	0.11±0.03
1983 M	Aphanopus carbo[b]	"	0.21±0.01
1984 M	Aphanopus carbo	"	0.51±0.17
1984 M	Aphanopus carbo	"	0.19±0.12
1984 M	Aphanopus carbo	"	<0.22[c]
1980 A	Epigonus telescopus	600	1.7±0.4
1980 P	Malacocephalus laevis	1000	<0.5[c]
1980 P	Deania calceus	1000	1.1±0.6
1982 M	Helicolenus dactylopterus	600	1.7±0.3
1982 M	Epigonus telescopus	600	1.1±0.3
1983 P	Centrophorus granulosus	400	<0.15[c]
1983 M	Helicolenus dactylopterus	600	0.44±0.38
1982 M	Sphyraena sphyraena	shal	0.45±0.20
1982 M	Sphyraena sphyraena	shal	0.46±0.04
1983 P	Lepidopus caudatus	200	0.86±0.04
1983 M	Thunnus thynnus	shal	0.79±0.05
1983 M	Sphyraena sphyraena	shal	0.26±0.16
1984 P	Lepidopus caudatus	200	0.70±0.48

[a] M: Madeira; A:Azores; P:west coast of Portugal

[b] Analysed by V.Noshkin, LLNL

[c] Lower detection limit at 90% confidence level; errors given are 1σ

3.3. Cesium-137

The results obtained for ^{137}Cs concentration in fish muscle are presented in Table 3. The analysed fish are grouped as follows: black scabbard; mid-depth species and shallow water fishes.

It can be seen that the ^{137}Cs concentrations are lower in the black scabbard than in other fish tissues, except the Sphyraena sphyraena. They are of the same order of magnitude as the ones reported by Mitchell & Pentreath (10) for the Coryphaenoides armatus in the north east Atlantic deep waters.

3.4. Polonium-210

The highest doses for marine organisms and for man through food consumption being due to ^{210}Po, their evaluation becomes important for us to know background doses and compare them with those resulting from artificial radionuclides. It is also helpful to be aware of ^{210}Po behaviour in the marine environment for understanding analog artificial radionuclides cycling.

Some preliminary results on total ^{210}Po concentration in different fish tissues are presented in Table 4. These results are not yet corrected for ^{210}Po ingrowth from ^{210}Pb present in the sample.

TABLE 4: ^{210}Po (total) concentrations in Fish tissues (mBq/g dry)
(Preliminary results not corrected for ingrowth from ^{210}Pb)

	MUSCLE	GONADS	LIVER	SKELETON
Sardina pilchardus	26(1)	-	1896(1)	43(1)
Trachurus trachurus	19±4(2)	118(1)	1229(1)	27(1)
Merluccius merluccius	45±16(2)	295(1)	-	31(1)
Scomber scombrus	6.1(1)	94(1)	1074(1)	12(1)
Raja undulata	3.4(1)	86(1)	99(1)	9.5(1) (cartilage)
Aphanopus carbo (Sesimbra)	0.5±0.1(3)	12(1)	16(1)	4.2(1)
Aphanopus carbo (Madeira)	1.0±0.9(2)	48±57(3)	22±13(4)	6.1(1)

Mean ± 1 standard deviation (nr of analysed specimens)

It can be seen that ^{210}Po concentrations in black scabbard fish tissues are significantly lower than those found in shallow water fish as well as in other deep slope fish.

4. CONCLUSIONS

Being the black scabbard a species which lives at depths of about 800-1400 m, It can be considered a potential pathway back to man for dumped radionuclides. Furthermore, this fisheries is economically important for Madeira population.

Although being classified as a benthopelagic fish, no specimens were were caught near the bottom: so, some doubts are arising about such classification.

Radionuclides concentrations in black scabbard tissues are lower than those found for other species from the same region, either from shallow waters or from deep slope. This seems to confirm that this species is not a benthic one.

ACKNOWLEDGEMENTS

Grateful acknowledgements are due to the Hydrographic Institute (Portugal) and the Regional Fisheries Laboratory (Madeira) for their cooperation in sample collection.

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STUDIES ON THE BIOACCUMULATION OF RADIONUCLIDES OF LONG HALF-LIFE IN MUSSELS IN THE NORTH EAST OF SPAIN

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Abstract

Water, sediments and mussels were analysed from areas in the NW of Spain, for ^{238,239,240}Pu, ^{137}Cs, ^{90}Sr. Sea depths were 24-65 m. Ranges of activity for seawater (pCi l^{-1}) were 0.138-0.335 for ^{90}Sr, 0.150-0.480 for ^{137}Cs, 0.140-0.190 for ^{60}Co. Levels of activities noted in sediments compared closely with those in the Mediterranean by other workers. In pCi kg^{-1} Pu figures were 5-96. Similarly for Mytilus edulis ^{239,240}Pu was 0.09-1.5 pCi kg^{-1} wet weight.

1. Introduction

Spain is a country with considerable coastline and there is so much possibility of alteration of the marine ecosystem due to nuclear type of incidents, that it is necessary to maintain a watch as far as possible on the levels of activity in the ecosphere.

We have selected the zone to the northeast of Spain for study both because it is representative for mussel culture, and because of its situation with respect to the Northeast Atlantic Trench.

2. Objectives in the first phase of the project

2.1 Collection of mussel samples (which are consumed by humans) in the Gallegas rivers as well as water and sediment samples/

2.2 Radioanalysis of the samples for ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{137}Cs which can arise from radioactive fallout, from the production of nuclear energy and the leaking of dumped radioactivity from the abyssal zone of the Atlantic.

3. Description of the investigation

3.1 Sampling areas

For the present study, the principal Gallegas rivers were selected; Vigo, Pontevedra, Arosa, Muros, La Coruna, Vivero.

3.2 Samples

The samples collected were water, sediment and Mytillus edulis

3.3 Methodology

3.3.1 Sampling and pretreatment

3.3.1.1 Water, Sediments

Sampling was done by the Boat B/O Lura. The coordinates (determined by radar techniques) are given in Table 1. The samples of water were obtained with Nansen-type bottles, provided with inversion thermometers, were filtered through a 20 micron filter and acidified to pH 1.5 with concentrated nitric acid. The salinity was determined in the laboratory with a salinometer calibrated against sea water of known conductivity. Oxygen concentrations were determined by a modified Winkler method. Sediment samples were taken either with a Van-Veen drag or hydraulic box-corer. The upper part was dried at 100° for 24 hours.

3.3.1.2 Mussels

At Vigo, Pontecedra, Arosa, La Coruna and Muros, sampling was done at various points, and three different depths. The Vivero mussels were collected by a sailor. They were wrapped in polyurethane foam and rapidly frozen at -20°C.

3.3.2 Method and technique of analysis

The determination of radioactivity was done by analytical procedures suited to detection of radionuclides at environmental levels, which included evaporation, drying, ashing etc.

3.3.2.1 Methods applied to the Mytillus edulis and sediment samples

-Gamma spectrometry. Gamma radioactivity was measured with coaxial Ge(Li) detectors with 25% eiffiency for ^{57}Co energies and resolution of 2.3 keV at 1173 keV. Spectra were accumulated with a Canberra-80 4000 channel multichannel analyser, and the SPECTRUM computer program was used for analysis.

-Plutonium. The samples were ashed at 600° to eliminate organic matter. The transuranics were dissolved in nitric acid and hydrogen peroxide, then precipitated with calcium oxalate. The precipitate was dissolved with 8M nitric acid and hydrogen peroxide. The solution was passed through a column of AG 1x8 resin to retain Pu. Then the Pu was eluted with 1.2M HCl containing H2O2.

The solution was evaporated and the eluted Pu electrodeposited in a NH_4OH medium at pH 4 onto discs of stainless steel of 25 mm diameter.

The counting was done by an alpha spectrometer with a solid-state detector of 300 mm^2 area and effeciency of 20%.

-Cesium. Cesium was separated as phosphomolybdate and then purified as a hexachloroplatinate. It was determined in a gas-flow counter with about 45% efficiency by its beta emission.

-Intercomparison. Intercalibration exercises were undertaken in conjunction with the International Laboratory of Marine Radioactivity at Monaco.

4.Results

Standard statistical treatments of the counting data were employed. The values obtained in the samples analysed are reflected in tables 2 to 6.

5. Conclusions

On viewing the results obtained in this first phase of the project, one is able to conclude that:

5.1 The methodology applied in collection, pretreatment and analysis of samples appears to be adequate.

5.2 The radiochemical methods applied for the obtaining of activities of cesium gave good yields.

5.3 The values obtained for water, sediments and mussels are similar to those reported by other authors on the same type of sample.

Table 1. Sampling coordinates

Location	Date	Coordinates	Sea Depth
Vigo	11.07.83	42° 13' 48"N 8° 47' 48"W	35m
Pontevedra	12.07.83	42° 23' 03"N 8° 45' 00"W	25m
Arosa	14.07.83	42° 33' 30"N 8° 54' 18"W	46m
Muros	05.08.83	42° 45' 18"N 9° 01' 00"W	35m
Coruna	02.08.83	43° 22' 18"N 8° 22' 03"W	29m
Vivero	27.09.83	43° 42' 18"N 7° 35' 42"W	27m
Vigo	14.11.83	42° 13' 48"N 8° 47' 48"W	43m
Pontevedra	10.11.83	42° 23' 03"N 8° 45' 00"W	32m
Arosa	10.11.83	42° 33' 30"N 8° 54' 18"W	65m
Muros	09.11.83	42° 45' 18"N 9° 01' 00"W	35m
Coruna	07.11.83	43° 22' 18"N 8° 22' 03"W	24m
Vivero	03.1 .83	43° 42' 18"N 7° 35' 42"W	24m

Table 2. levels of activity in sea water (pCi/l)

	Sr-90	Cs-137	Co-60
VIGO	----	0.170 ± 0.030	0.140
PONTEVEDRA	0.138 ± 0.042	0.150 ± 0.020	0.190
AROSA	0.217 ± 0.055	0.170 ± 0.020	----
MUROS	----	0.170 ± 0.020	0.150
LA CORUÑA	----	----	----
VIVERO	0.335 ± 0.063	0.480 ± 0.050	0.180

Table 3. Levels of activity in sediments (pCi/kg dry weight)

	Cs-137	Pu-239, 240	Cs/Pu
VIGO	380 ± 10	16 ± 11	24
PONTEVEDRA	440 ± 10	96 ± 15	4.6
AROSA	240 ± 10	51 ± 10	4.7
MUROS	280 ± 10	40 ± 17	7
LA CORUÑA	16 ± 2	22 ± 4	0.7
VIVERO	15 ± 2	5 ± 3	3

Table 4. Levels of activity in edible part of Mytillus edulis (pCi/kg wet weight

	Cs-137	Pu-239, 240	Pu-238
VIGO	6.0 ± 2.2	0.09 ± 0.05	< 0.1
AROSA	6.5 ± 2.4	0.1 ± 0.1	< 0.4
LA CORUÑA	6.7 ± 2.2	0.57 ± 0.08	< 0.1
VIVERO	6.5	1.50 ± 0.03	< 0.5

Table 5. Comparison between the levels of activity of Cs and Pu found in sediments (pCi/kg dry weight

Location	Depth (m)	Pu	Cs/Pu	Worker
Ligurian Sea	12	32	12.5	Jennings (1984)
Ligurian Sea	45	17	16.7	"
Ligurian Sea	93	27	14.3	"
COSTAS GALLEGAS:				
Vigo	33	16	24	JEN (1984)
Pontevedra	24	96	5	"
Arosa	44	51	5	"
Muros	33	40	7	"
La Coruña	22	22	0.5	"
Vivero	25	5	3	"

Table 6. Comparison of levels of activity in Mytillus edulis in Mediterranean and Atlantic (pCi/kg wet weight)

Location	Sampling date	Pu-239, 240	Worker
MEDITERRANEAN			
Mónaco	November 1976	0.39 ± 0.04	Ballestra
Saint Mandrier	June 1976	0.15 ± 0.02	"
Martigues Ponteau	" "	0.20 ± 0.03	"
Port de Bouc	" "	0.06 ± 0.01	"
Port Saint-Louis	" "	0.09 ± 0.01	"
" " "	May 1977	0.23 ± 0.02	"
Gran du Roi	June 1976	0.11 ± 0.02	"
Séte (Port)	" "	0.17 ± 0.02	"
"	May 1977	0.11 ± 0.02	"
" (étans)	" "	0.12 ± 0.04	"
Banyuls	June 1976	0.61 ± 0.07	"
Venezia	May 1977	0.11 ± 0.02	"
ATLANTIC			
Vigo	June, Dec 1983	0.09 ± 0.05	JEN
Arosa	" " "	0.1 ± 0.1	"
La Coruña	" " "	0.57 ± 0.08	"
Vivero	" " "	1.50 ± 0.03	"

LONG-LIVED RADIONUCLIDES IMPORTANT IN MARINE WASTE DISPOSAL

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Abstract

The calculation starts with high level waste and tabulates results for time periods of 0, 100,10,000 and a million years. The assumed relative activity figures are divided by the Allowable Limit of Intake to give potential risk figures. The figures are further adjusted by a factor related to K_d which allows for the fact that most activity for some radionuclides will be adsorbed onto sediments. Similarly a further adjustment is made to the figures to allow for the different concentration factors for radionuclides likely for the biota which are the probable route to man. In the period 100-10000 years the following radionuclides then predominate; ^{137}Cs, ^{90}Sr, ^{241}Am, ^{243}Am, ^{240}Pu, ^{239}Pu, ^{237}Np, ^{99}Tc, ^{93}Zr, ^{244}Cm. Future research projects should therefore concentrate on these isotopes. Especially little information seems available for ^{93}Zr and ^{237}Np.

1. METHODS FOR IDENTIFICATION OF IMPORTANT NUCLIDES

1.1. Inventories

The disposal of high-level waste to the seabed presents the most important potential source of radioactive marine pollution. Our study shall be limited to this source alone. Baxter [1] has made a list of those radionuclides which contribute over 97% of the total activity present at various timepoints after disposal. Table 1 shows the inventories in TBq (10^{12}Bq), assuming a mean lapse of 10 years prior to disposal.

The wastes arising in Table 1 are those to be expected from a global nuclear capacity of 2500 GW by the early to mid-21st century. However, the absolute amounts of waste are not important in the present context. It is the relative levels of the various radionuclides, which are of interest.

1.2. Potential impact

In order to estimate the potential radiological impact of the waste we may divide the figures in Table 1 with the ALI values [2] for the various radionuclides as given in Table 2.

Table 1. High activity waste arisings and post-disposal activities (TBq) (adopted from Baxter [1].

Timepoint (yr)											
0			10^2			10^4			10^6		
30y	^{137}Cs	1.3x10^9	30y	^{137}Cs	1.3x10^8	2x10^5y	^{99}Tc	2x10^5	10^6y	^{93}Zr	1.8x10^4
29y	^{90}Sr	8.9x10^8	29y	^{90}Sr	7.4x10^7	7x10^3y	^{243}Am	1.1x10^5	2x10^5y	^{99}Tc	7.8x10^3
2y	^{134}Cs	1.1x10^8	90y	^{151}Sm	7.4x10^6	7x10^3y	^{240}Pu	4.8x10^4	2x10^6y	^{237}Np	4.1x10^3
2.6y	^{147}Pm	1.0x10^8	432y	^{241}Am	2.2x10^6	10^6y	^{93}Zr	2.8x10^4	3x10^6y	^{135}Cs	3.1x10^3
8.6y	^{154}Eu	6.7x10^7	8.6y	^{154}Eu	8.9x10^5	2x10^4y	^{239}Pu	1.8x10^4	7x10^6y	^{107}Pd	1.5x10^3
18y	^{244}Cm	2.5x10^7	88y	^{238}Pu	6.7x10^5	10^5y	^{126}Sn	7.8x10^3	1.6x10^7y	^{129}I	5.2x10^2
90y	^{151}Sm	1.6x10^7	18y	^{244}Cm	4.8x10^5	7x10^4y	^{79}Se	5.2x10^3	2x10^5y	^{234}U	7.4x10^1
2.7y	^{125}Sb	9.3x10^6	7x10^3y	^{243}Am	2.7x10^5	2x10^6y	^{237}Np	5.9x10^3	4x10^9y	^{238}U	4x10^1

Table. 2. Number of ALI values (divided by 10^{12}) in the high activity waste arisings in Table 1.

Timepoint (yr)							
0		10^2		10^4		10^6	
^{90}Sr	9x10^2	^{90}Sr	7x10^1	^{243}Am	2x10^0	^{237}Np	1x10^0
^{137}Cs	3x10^2	^{241}Am	4x10^1	^{237}Np	2x10^0	^{129}I	3x10^{-3}
^{244}Cm	3x10^2	^{137}Cs	3x10^1	^{240}Pu	2x10^{-1}	^{93}Zr	4x10^{-4}
^{134}Cs	4x10^1	^{244}Cm	5x10^0	^{239}Pu	9x10^{-2}	^{234}U	2x10^{-4}
^{154}Eu	3x10^0	^{243}Am	5x10^0	^{99}Tc	2x10^{-3}	^{135}Cs	1x10^{-4}
^{147}Pm	5x10^{-1}	^{238}Pu	2x10^0	^{126}Sn	8x10^{-4}	^{99}Tc	8x10^{-5}
^{125}Sb	1x10^{-1}	^{154}Eu	4x10^{-2}	^{93}Zr	6x10^{-4}	^{238}U	5x10^{-5}
^{151}Sm	3x10^{-2}	^{151}Sm	1x10^{-2}	^{79}Se	3x10^{-4}	^{107}Pd	2x10^{-6}

1.3. Radioecological marine index

If the radionuclides escape from the waste containers to the the sediments, the amount of activity entering the water is influenced by the magnitude of the K_d for pelagic sediments. The transfer from water to human marine food chains is determined by the concentration factors (CF) from water to fish and shellfish. The International Atomic Energy Agency has recently made a review of sediment K_d's and cocentration factors [3]. We will define a "Radiological Marine Index" for the radionuclides in the waste as the ratio CF/K_d. As CF we shall use the consumption weighted CF for fish, crustaceans and molluscs. The total global catch of fish in 1980 was 56 M tons and of crustaceans and molluscs 3.4 and 5 M tons, respectively [4]. In Table 3 the CF/K_d ratios are calculated for the radionuclides mentioned in Table 1.

Table 3. Radioecological Marine Index (CF/K_d) for elements in the high-activity waste arisings in Table 1.

Se	$6x10^0$	U	$8x10^{-3}$
Tc	$2x10^0$	Pu	$3x10^{-3}$
Sn	$1x10^0$	Cm	$2x10^{-3}$
Sb	$8x10^{-1}$	Am	$1x10^{-3}$
Pd	$6x10^{-2}$	Pm	$9x10^{-4}$
Cs	$5x10^{-2}$	Sm	$9x10^{-4}$
Np	$5x10^{-2}$	Zr	$8x10^{-4}$
I	$5x10^{-2}$	Eu	$2x10^{-4}$
Sr	$1x10^{-2}$		

1.4. Marine risk index

In order to calculate a "Marine Risk Index" we may multiply the number of ALI values from Table 2 with the corresponding Index values in Table 3 as shown in Table 4.

Table 4. "Marine Risk Index" values: $\frac{\text{Inventory}}{\text{ALI}} \times \frac{CF}{K_d}$

Timepoint (yr)							
0		10^2		10^4		10^6	
^{137}Cs	$2x10^1$	^{137}Cs	$2x10^0$	^{237}Np	$1x10^1$	^{237}Np	$5x10^{-2}$
^{90}Sr	$9x10^0$	^{90}Sr	$7x10^{-1}$	^{99}Tc	$4x10^{-3}$	^{99}Tc	$2x10^{-4}$
^{134}Cs	$2x10^0$	^{241}Am	$4x10^{-2}$	^{243}Am	$2x10^{-3}$	^{129}I	$2x10^{-4}$
^{244}Cm	$6x10^{-1}$	^{244}Cm	$1x10^{-2}$	^{79}Se	$2x10^{-3}$	^{135}Cs	$5x10^{-6}$
^{125}Sb	$8x10^{-2}$	^{238}Pu	$6x10^{-3}$	^{126}Sn	$8x10^{-4}$	^{234}U	$2x10^{-6}$
^{154}Eu	$6x10^{-4}$	^{243}Am	$5x10^{-3}$	^{240}Pu	$6x10^{-4}$	^{238}U	$4x10^{-7}$
^{147}Pm	$5x10^{-4}$	^{151}Sm	$9x10^{-6}$	^{239}Pu	$3x10^{-4}$	^{93}Zr	$3x10^{-7}$
^{151}Sm	$3x10^{-5}$	^{154}Eu	$8x10^{-6}$	^{93}Zr	$5x10^{-7}$	^{107}Pd	$1x10^{-7}$

1.5. Marine CF-risk index

If we disregard the absorption on sediments we may calculate a so-called "Marine CF Risk Index", as shown in Table 5.

Table 5. "Marine CF Risk Index" values: $\frac{\text{Inventory}}{\text{ALI}} \times \text{CF}$

Timepoint (yr)							
0		10^2		10^4		10^6	
^{244}Cm	$9x10^5$	^{241}Am	$8x10^4$	^{243}Am	$4x10^3$	^{237}Np	$5x10^1$
^{137}Cs	$3x10^4$	^{244}Cm	$2x10^4$	^{237}Np	$1x10^2$	^{93}Zr	$2x10^{-1}$
^{134}Cs	$4x10^3$	^{243}Am	$1x10^4$	^{240}Pu	$6x10^1$	^{129}I	$3x10^{-2}$
^{154}Eu	$3x10^3$	^{137}Cs	$3x10^3$	^{126}Sn	$4x10^1$	^{99}Tc	$2x10^{-2}$
^{90}Sr	$2x10^3$	^{238}Pu	$6x10^2$	^{239}Pu	$3x10^1$	^{135}Cs	$9x10^{-3}$
^{147}Pm	$5x10^2$	^{90}Sr	$1x10^2$	^{79}Se	$2x10^0$	^{234}U	$8x10^{-4}$
^{125}Sb	$4x10^1$	^{154}Eu	$4x10^1$	^{99}Tc	$4x10^{-1}$	^{107}Pd	$6x10^{-4}$
^{151}Sm	$3x10^0$	151Sm	$9x10^{-1}$	^{93}Zr	$2x10^{-1}$	^{238}U	$2x10^{-4}$

2. DISCUSSION

The tables in the previous chapter may be used to identify those long-lived radionuclides, which are most important in the context of marine waste disposal.

If we base our indentification on inventories alone we use Table 1. It is unlikely that any waste disposed in the deep ocean will reach man before several years have elapsed after the disposal. We may further argue that if the waste first enters the human food chain after one million years the doses received at that time should have much less weight than those received now, and we may therefore neglect them. This leaves us with the time span from 10^2 to 10^4 years. The important nuclides then becomes ^{137}Cs, ^{90}Sr (for the 10^2 year case) and ^{99}Tc, ^{243}Am, ^{240}Pu, ^{93}Zr, and ^{239}Pu (for the 10^4 year case).

If we include the ALI values in our evaluation as shown in Table 2, the important nuclides in the two cases become ^{90}Sr, ^{241}Am and ^{137}Cs and for 10^4 year: ^{243}Am and ^{237}Np.

If we include, furthermore, the environmental behaviour of the radionuclides as shown in Table 4, we get for the 10^2 year case: ^{137}Cs and ^{90}Sr as the important nuclides and for the 10^4 year case: ^{237}Np.

If we disregard the absorption on sediments, Table 5 shows that ^{241}Am, ^{244}Cm, and ^{243}Am become the important radionuclides for the 10^2 year case and ^{243}Am and ^{237}Np for the 10^4 year case.

If we combine the various methods of identification the following radionuclides seem to be important: ^{137}Cs, ^{90}Sr, ^{241}Am, ^{243}Am, ^{240}Pu, ^{239}Pu, ^{237}Np, ^{99}Tc, ^{93}Zr, and ^{244}Cm.

The importance of some of these radionuclides are influenced by the ALI, K_d and CF values. As regards the ALI values, Harrison [5] has recently shown that the ALI value for ^{237}Np may be a factor of ten too low, while that of ^{239,240}Pu may be 5 times too high. This will not change the importance of ^{237}Np in Table 4, but it will make ^{237}Np less important than ^{239,240}Pu in Table 5, where the influence of K_d has been neglected.

The K_d and CF values are encumbered with considerable uncertainties. The range of the values for a given element will typically be 2 orders of magnitude [3]. Two of the radionuclides in our list: ^{237}Np and ^{93}Zr have a K_d range 3 orders of magnitude, and in the case of ^{237}Np the range of CF for fish is the same.

3. CONCLUSION

Future research projects on radionuclides associated with deep sea disposal of high-level radioactive waste should deal with the following radionuclides: ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{137}Cs, ^{237}Np, ^{239,240}Pu, ^{241}Am, ^{243}Am and ^{244}Cm.

As the information on the environmental behaviour of ^{93}Zr, and in particular, ^{237}Np is low, the research activity should focus on these radionuclides.

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