IAEA-TECDOC-301

THE BEHAVIOUR OF RADIUM IN WATERWAYS AND AQUIFERS

FINAL REPORT OF THE
CO-ORDINATED RESEARCH PROGRAMME ON
SOURCE, DISTRIBUTION, MOVEMENT AND DEPOSITION OF RADIUM
IN INLAND WATERWAYS AND AQUIFERS
SPONSORED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

In 1975, radium was known to be a significant contaminant in the liquid and solid wastes from uranium mining and milling and so the IAEA began a coordinated research programme on "The source, distribution, movement and deposition of radium in inland waterways and aquifers".

The primary aim of this coordinated research programme was to produce a report on radium behaviour in the aquatic environment from the point of view of health protection. It was no easy matter to draft this report as each principal author of a chapter was required to submit an integrated report on the work produced by the other laboratories participating in the programme and to place all of this in the context of the work published in the literature.

All the authors set about doing this on the basis of the data available to them at the time, and the chapters thus forced together can in general, albeit with varying degrees of success, be considered to cover the most important aspects of the subject.

Technical and administrative aspects are dealt with in the relevant chapter, so at this point we shall only mention that the Scientific Secretaries were, successively: P.A. Bonhote (1975-1976), L. Farges (1976-1979) and R. Kirchmann (1980).

It is hoped that the data produced by the various laboratories participating in the programme will be of great value to those authorities responsible for assessing the consquences of radium releases to inland waters and to those responsible for setting discharge limits.

René KIRCHMANN
1982-10-01

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PREFACE

At the first coordination meeting of this Coordinated Research Programme, "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers" (CRP Radium 1), the participants agreed that a joint report should be published at the end of the programme - indeed, a preliminary outline of the contents of the final report was drawn up. It was for this reason that the participants decided at the fourth and last coordinating meeting to produce the present document.

The following procedure was adopted at that meeting: two editors - the Scientific Secretary at the time (R. Kirchmann) and the Chairman of the last meeting (A. Williams) - were to be responsible for putting together the different contributions from certain participants who would act as principal authors.

The two editors circulated a letter to the authors in which they made recommendations regarding the essential points to be dealt with in the chapters submitted, and provided references and reports on the subject which they had available at the time.

The first draft comprising eight scientific chapters was thus prepared and discussed at a meeting of the group held during the Knoxville symposium in July 1981. In the light of the contributions and in order to avoid repetition, the two editors felt at that time that an attempt should be made to recast the report.

The second, remodelled draft aimed at being a type of monograph on the subject. Unfortunately, this attempt was not supported unanimously by the participants, who did not wish to accept the arrangement proposed by the editors. In addition, there proved to be fundamental shortcomings which it has not yet been possible to remedy.

It is for these reasons that, in conjunction with the authors, the Agency's Secretariat, represented by Mr. J. Molinari, in charge of the Agency's radium programme, took the following decisions:

(a) Each chapter foreseen in the first draft would be published under the sole responsibility of its principal author, who could at any time call on the assistance of a colleague who had participated in the programme if he felt it necessary;

(b) In view of the number and extent of the shortcomings and of the diversity of the information gathered, the document should be published in the form of a TECDOC, instead of a Technical Report as initially planned;

(c) The present document constitutes a framework of a kind for a future report to be written at the end of the new coordinated research programme (CRP), entitled "Environmental migration of radium and other contaminants present in liquid and solid wastes from the mining and milling of uranium" (CRP Radium II), whose first meeting was held in Ottawa, 17-21 May 1981.

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[1] In conjunction with the authors.

[2] Represented by J. Molinari, successor in charge of the Agency's radium programme.

It is with this in mind that each chapter of this document is preceded by an editor's note intended to bring out both the chapter's good points and shortcomings as well as to make a number of useful suggestions concerning the future report, which is to be the highlight of this coordinated programme - a programme in which a number of prominent laboratories have so actively participated for many years.

This report being considered by the Secretariat as well by the authors as a working document, observations, comments and additional data will be welcomed and should be addressed to:

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"Radium 1"
(from 1980-01-01 to 1981-08-31)

Jacques MOLINARI
Project Officer of the CRP
"Radium 2"
(from 1981-09-01)

HISTORY

- 16-20 June 1980
  Fourth and last Research Coordination Meeting (RCM) of the Coordinated Research Programme (CRP) "Radium 1" (Scientific Secretary, R. KIRCHMANN)
- 16 December 1980
  Circular letter from the Scientific Secretary (R. KIRCHMANN) to each participant requesting each contributor of the final report to produce a specific chapter with cooperation of other participants if needed, with the final version being co-edited by A. WILLIAMS and R. KIRCHMANN
- 30 August 1981
  During the IAEC/CEC/OECD-NEA International Symposium on Migration in the Terrestrial Environment of the Long-lived Radionuclides from the Nuclear Fuel Cycle, Knoxville, a meeting of a group of CRP participants was realized [A. WILLIAMS (Australia), P. BENES (CSSR), N. FOURCADE (France), D. VAN AS (South Africa), M.L. MARPLE (U.S.A.), P. STEGNAR (Yugoslavia)] to exchange information on the first draft, followed with a review by A. WILLIAMS and R. KIRCHMANN of this first draft in order to produce a second draft to be circulated to all participants
- 15 April 1982
  Second draft, result of the modifications made by the co-editors of the original chapters in an attempt to realize a monograph, sent for comments to authors, and for information to participants of the first RCM of the CRP "Radium 2" (J. MOLINARI, Technical Officer)
- 17-21 May 1982
  At the first RCM of the CRP "Radium 2", was arranged a meeting of a group of participants from the CRP "Radium 1" [A. PASCHOA (Brazil), P. BENES (CSSR), N. FOURCADE (France), KUROKAWA (Japan), M.L. MARPLE (U.S.A.)] to exchange information on the second draft. (J. MOLINARI, Scientific Secretary)
- 16 June 1982
  Circular letter to all participants of CRP "Radium I" and CRP "Radium II". Taking into account the comments received and considering the difficulties in integrating and harmonizing the various contributions, the Technical Officer, J. MOLINARI informs authors and participants that decision was taken to discontinue the edited monograph and to produce instead, as a TECDOC, the chapters prepared by the authors under their sole responsibility
- 29-30 September 1982
  Reconstitution by R. KIRCHMANN, as IAEA consultant, of the chapters in their previous format, and agreement with the Scientific Secretary (J. MOLINARI) on the final shape of the report
- 6 May 1983
  Dispatch to each author of the retyped version of manuscripts accompanied by editorial comments (J. MOLINARI)
- 8 September 1983
  Reception of the last author's correction.

INTRODUCTION

Radium is element 88 in group IIA of the Periodic Table. It can exist in the form of 25 different isotopes, none of which are stable. Among the naturally occurring isotopes, Ra-226 (α-emitter, half-life $\sim$1600 years and Ra-228 (β-emitter, half-life 5.8 years) are the most abundant, being daughters of the naturally most abundant isotopes of uranium (U-238) and thorium (Th-232) respectively. From the health point of view the two are also the most radiotoxic; when they are ingested over a long period of time they deliver the highest radiation doses to bone, where radium tends to be accumulated.

Because uranium is the basis of the present nuclear industry, Ra-226 is the most important isotope for present concern, and this report deals almost exclusively with this isotope. The other naturally occurring isotopes are Ra-223 (α-emitter, half-life 11.4 days) coming from U-235, and Ra-224 (α- and γ -emitter, half-life 3.6 days) coming also from Th-232.

Radium was first discovered in 1898 by Marie and Pierre Curie who isolated it from the uranium ore, pitchblende (Curie et al. 1898). It was subsequently used extensively in medicine and in industry as a source of radiation because it has a high specific activity. Thus, from its discovery up until World War II, uranium ores were mined primarily for their radium content. Uranium has also been mined since Renaissance times, in association with silver, at Jachymov in Czechoslovakia, where the oxide was used as a glazing pigment. During World War II, uranium developed military and energy value and, since then, it has been mined extensively on every continent, with the associated radium usually being discarded with the tailings.

Radium was first identified as a significant environmental pollutant from the uranium industry in the 1950's by Tsivoglou and others working in the Colorado Plateau area of the U.S.A. (Tsivoglou et al. 1958). In the early 1960's, Havlik reported significant radium pollution from uranium mining in Czechoslovakia (Havlik 1970 with references) and Kirchmann et al. (1973 with references) reported radium pollution from a radium extraction plant and a phosphate mill in Belgium. Since then significant radium pollution has been identified in many other places, coming from uranium, phosphate and even gold mining and milling operations, and from coal ash.

The early impetus for considering radium to be the most radio-toxic daughter product of uranium and thus the most critical in managing uranium wastes, was the ingestion limits for radionuclides set by the International Commission on Radiological Protection (ICRP) in 1959 (ICRP 1960). The maximum permissible concentration for Ra-226 was set 10 times lower than that of any other long-lived uranium daughter, and 200 times lower than the least restrictive one (Th-230). This very restrictive limit was based on a simple exponential uptake and retention model which indicated a long residence time for radium in human bone (44 years biological half-life). However in reviewing the data on human retention of the alkaline earth elements, Marshall et al. (ICRP 1973) developed a more complex model in which the initial rate of loss from bone was much more rapid than previously thought, and the rate of loss decreased with time. The subsequently revised ICRP ingestion limits (ICRP 1979-80) now put all four of the long-lived uranium daughters (Th-230, Ra-226, Pb-210, Po-210) within a range of a factor of 5 of each other, with Ra-226 now being the second restrictive nuclide following Pb-210.

This report on radium is the outcome of international concern for responsible management of uranium mine and mill wastes. Its scope appears somewhat narrow from the point of view of health protection; however the material covered here is at least necessary, if not sufficient, to this end. As the first monograph of its kind on the environmental behaviour of long-lived uranium daughters, it points the way to the further work that needs to be done.

Alex WILLIAMS

Chapter 1

RADIUM: A HISTORICAL INTRODUCTION AND OVERVIEW

1.1. THE DISCOVERY OF RADIUM

The discovery of radium in 1898 was the result of an intensive research program by Marie and Pierre Curie. During her systematic investigation of possible photographic emissions from many substances, Mme. Curie observed that the activity of the uranium ore pitchblende was about four times as great as the uranium it contained. She thought the ore must contain some substance with a much higher activity. Working at the Sorbonne in Paris, the Curies obtained two highly radioactive elements (M. Curie, P. Curie & Bémont, 1898) - polonium and radium, by a chemical separation based on relative activities of these elements. The much higher activity of radium allowed it to be traced throughout the process by its stronger ionizing effects.

In 1902 using approximately 5 tons of pitchblende residues from the mines at Joachimsthal in Czechoslovakia, Mme. Curie separated radium from the barium it was associated with. Working in poor conditions, she laboured long and hard, finally arriving at the first pure salt, radium chloride, by a fractional crystallization method (M. Curie, 1902). This technique was later modified to yield the bromide.

The commercial production process is similar to that used by the Curies, and for this purpose Pitchblende was later mined in rich deposits in the Congo and Canada while carnotite from Colorado was the US source. The name radium was originally used only for the most stable isotope (226) but now represents element 88 of the periodic table. Radium-226 has a relatively long half-life of 1600 years. Its high activity is indicated by the luminosity observed by the Curies.

In 1899 they observed "induced" radioactivity in solid substances placed near radium (P. & M. Curie, 1900) that, later, Dorn explained in terms of "radium emanation" (radon gas Rn). Radium itself was found to be 2 million times as active as uranium, emitting α, β and γ radiation when in equilibrium with Rn, its daughter element. In 1910 M. Curie and A. Debierne prepared the pure metal by electrolysis of the fused salt (M. Curie and Debierne, 1910). In 1911 she was awarded a Nobel Prize, her second, in chemistry.

The discovery of radium was largely responsible for the volume of research into radioactivity that followed, with experiments on its spectroscopic, physical and chemical properties e.g. hydrolysis of water (M. Curie, 1925). Other radioactive elements were found and investigations by Thomson, Soddy and Rutherford, among others, on emissions enhanced the understanding of matter.

1.2. USING THE PROPERTIES OF RADIUM

The recognition of radium as a source of therapeutic radiation dates from Becquerel. He noticed a burn on his skin adjacent to where he carried a vial of radium in his vest pocket. Pierre Curie deliberately induced a similar burn on his arm which was identified by a dermatologist as being analogous to X-ray burns. Thus a therapeutic use similar to

X-rays (in use for several years) seemed logical. The Curies supplied dermatologists in Paris with radium who used it to treat skin cancers. Using filters to emit only γ radiation, Dominici buried large tubes in growths. Regaud by 1910 had developed the use of smaller amounts in needles which were implanted interstitially. Later he used radium as a source in a "bomb" apparatus, for external administration. Other medical uses included treatment of certain psychoses by implantation in the brain, as a source of localised radiation. This practice was soon abandoned.

Another major early use was in luminescent paints for clock and meter dials; by mixing with an inert scintillator e.g. ZnS and a lacquer. This resulted later in many cases of occupational cancer from ingestion of paint or radon, due to the lack of safety precautions and the method of applying the paint (Evans, 1933).

Later industry used radium in radiography for determination of thickness of flaws in rolled or cast metal. This entailed enclosure of radium in concentric spheres of inert material e.g. Fe, Al, Ag or more recently platinum/iridium alloy. Radium was also incorporated into manufacture of static electricity eliminators and electronic valves. In all the above cases, radium was used in the bromide or sulphate form. However now it is largely replaced by substitutes owing to the dangers we are now aware of. Radium combined with beryllium is used as a neutron source in limited amounts for research, material analysis and oil-well mapping.

1.3. AWAKING TO THE CONSCIENCOUSNESS OF DANGERS

1.3.1. Realizing Health Hazards of Radium

Although a slow and lethal poison when administered internally, correct procedures gave radium a prominence in radiology. However the dangers of exposure were realised only after some time (Evans, 1933, Laborde, 1911). Early workers, patients and even Marie Curie succumbed to the effects of the new substance. Although both she and her husband had their hands badly burnt and were in chronic ill-health, Mme. Curie was apparently reluctant to admit the dangers of radium.

Observations upon the occupational health hazard of radium were originally made with workers in the luminescent paint industry. Many who used their lips to form pointed ends on their brushes were later found to be suffering from necrosis of the jaw or cancer of the mouth. This often proved fatal (Flinn, 1926; Martland, 1929). Radium dial painting was the first area to indicate the more acute dangers of radium ingestion. This was the only large scale contact by workers at this time, so it is not surprising to note a relative lack of warnings in the early literature. The radiological use of X-rays pointed to the dangers therein earlier, so protection standards had been put forward. Studies on workers, volunteers, animals and plants revealed such severe consequences as gamma burns, cancers of skin and bone, pernicious anaemia, hemolysis, sterility and others.

Quite early, laboratory safety was questioned (Eve, 1905) and studies demonstrated the persistence of Ra in body tissue, especially bone (Meyer, 1906; Pusey, 1911; Dominici and Faure-Beaulieu, 1910; Dominici, Petit and Jaboin, 1910 and 1911). Carcinogenesis involving radium was then illustrated (Brancati, 1926; Daels and Bacten, 1926).

These hazards created considerable scientific interest in the field of medicine, and in control of paint activity (Schlundt, Barker and Flinn, 1929). Following on from earlier X-ray safety proposals, the British X-ray and Radium Protection Committee was established in 1921. This disparity was largely due to cancer surgeons using radium while more experienced radiologists used X-rays. By the end of the decade similar American and international bodies were set up. These bodies advised on tolerance or maximum permissible doses (MPD) per day or year, of radiation. Clinical procedures were put forward to ensure safety for both patient and worker. However, these doses have been progressively lowered as detection equipment became more sensitive to damage over long and short terms. For example:

Year	Body	MPD (rem/day)
1926	Solomon	2.0
1928	Barclay & Cox	0.04
1928	BXR Comm.	0.2
1932	Failla	0.1
1934	ICRP	0.2
1936	NCRP	0.1
1949	NCRP	0.05
1950	ICRP	0.05 (.3 rem/week)
1957	NCRP	0.0014 (1.4x10^{-3})

(Modified after Braestrup & Wyckoff, 1958)

MPD : Maximum permissable dose
BXR Comm. : British X-ray and Radium Protection Commission
ICRP : International Commission on Radiological Protection
NCRP : National Council on Radiation Protection

1.3.2. Considering Environmental Effects of Radium

The effect of radioactive elements within the environment was not considered until after the second world war. With the realisation of the scale of "fallout" from nuclear weapons testing, researchers began to trace the fate of ^{90}Sr and ^{131}I in food chains. However, in aquatic studies, radium was considered to be merely a naturally occurring radionuclide, with little impact (Rona and Urry, 1962).

In the fifties however, E.C. Tsivoglou worked on the problem of water pollution from uranium milling wastes (Tsivoglou et al. 1956, 1958) and in particular on the Animas River in New Mexico (Tsivoglou et al.

1959, 1960). In these studies Ra was identified as a major waste, occurring in tailings piles dumped around the site, which led to dangerous levels in the river water. Radium has a prominence in environmental studies of proposed U-mining sites, and its pathway through the biosphere has been studied (Havlik et al 1968 and 1973). As a result, measures for stabilizing tailings piles and control of leakage to rivers were put forward (U.S. Dept. of HEW, 1962).

REFERENCES

BECQUEREL H. & CURIE P., Compt. Rend. 132 p. 1287 (1901).

BETT T.H., "On a fatal pulmonary fibrosis from Industrial Radium Injury" Frankfurt Z. Path., 42, 170-87 (1931).

BRAESTRUP C.B. & WYCKOFF H.O., in "Radiation Protection" Charles C. Thomas, Springfield (1958).

BRANCATI R., "Experimental Production of Rare Tumours by Stimulation (tar and radium)" Bull. Atti Accad. Med. Roma, (2), 52, 47-52 (1926).

BRUES A.M., LISCO H., & FINKEL M., "Carcinogenic Action of some Substances which may be a problem in certain future industries" Radiology, 49, 361-3 (1947) (MDDC-145).

CURIE M., CURIE P. and BEMONT G., "Another new Radio-active Element" Compt. Rend., 127, 1215-17 (1898).

CURIE M. and DEBIERNE A., "Metallic Radium". Compt. Rend., 151, 523-5 (1910).

CURIE M., "Atomic Weight of Radium" Compt. Rend., 135, 161-3 (1902).

CURIE M. & CURIE P., "Radioactive Bodies" Bull. Soc. Franc. Phys., 142, 6 (1900).

DAELS F. & BACTEN G., "A Note on the Different Kinds of Malignant Tumors Experimentally obtained by means of radium", Lancet, 211, 666-9 (1926).

DOMINICI H., PETIT G. & JABOIN A., "The Existence and Applications of Radioactivity Persisting in the Organism after Intravenous Injection of an insoluble salt of radium" Compt. Rend., 150, 726-8 (1910).

DOMINICI H., PETIT G. & JABOIN A., "Persisting Radioactivity of Organism under Influence of Injection of Insoluble Ra Compounds. Radioactive Serotherapy" Compt. Rend., 153, 1509-11 (1911).

DOMINICI H. & FAURE-BEAULIEU M., "The Arrest and the Prolonged Story of Radium in the Living Tissues for a Period Exceeding a Year" Compt. Rend. Soc. Biol., 68, 46-8 (1910).

EVANS R.D., "Radium Poisoning. A Review of Present Knowledge" Am. J. Pub. Health, 23, 101-123 (1933).

EVE A.S., Infection of Laboratories by Radium", Nature, 71, 460-1 (1905).

FLINN F.B., "Radioactive Material & Industrial Hazard?" J. Am. Med. Assoc., 87, 2078-81 (1926).

HAVLIK B., GRAFOVA J., NYCOVA B., "Ra^{226} Liberation from Uranium ore Processing Mill Waste Solids & Uranium Rocks into Surface Streams - I". Health Physics, 14, 417-422 (1968).

HAVLIK B. & ROBERTSON E., "Radium uptake by F.W. Algae", Hygiene, Epiderm, Micro & Immunology, 17, 393-405 (1973).

MARTLAND H.S., "Occupational poisoning in manufacture of luminous watch dials", J.A.M.A., 92, 466-73, 552-59 (1929).

MEYER M., "The Fate of radium after its introduction in the animal organism, with some remarks on excretion of barium", J. Biol. Chem, 2, 461-79 (1906).

PUSEY W.A., "Biological effects of radium", Science, 33, 1001-5 (1911).

RONA E. & URRY W.D., "Radioactivity of ocean sediments VIII Radium and uranium content of ocean and river waters" Am. J. Sci., 250, 241-262 (1962, April).

SCHLUNDT H, BARKER H.H., & FLINN F.B., "The detection and estimation of Mesothorium in living persons" Am. J. Rotengenol Radium Therapy, 21, 345-54 (1929).

SILBERSTEIN H.E., "Radium Poisoning. A survey of the literature dealing with the toxicity and metabolism of absorbed radium", (1945) University of Rochester, AECD-2122, 41 p (1945).

TAYLOR L.S., "Radiation Protection Standards" CRC London 1971, Butterworth.

TSIVOGLOU E.C., BARTSCH A.F., RUSHING D.E., HOLADAY D.A., (U.S. Pub. Health Service) "Effects of Uranium Ore Refinery Wastes on Receiving Waters, Sewage and Industrial Wastes", 30, 8, 1012 (1958).

TSIVOGLOU E.C., BARTSCH A.F., RUSHING D.E., HOLADAY D.A., "Report of Survey of Contamination of Surface Waters by Uranium Recovery Plants". U.S. Public Health Service, R.A., Taft Sanitory Engineering Centre, Cincinnati, Ohio (1956).

TSIVOGLOU E.C., SHEARER S.D., SHAW R.M., JONES J.D., ANDERSON J.B., SPONANGLE C.E., CLARK D.A., "Survey of Interstate Pollution of the Animas River, Colorado-New Mexico". U.S. Public Health Service, R.A. Taft Sanitary Engineering Centre, Cincinnati, Ohio (1959).

TSIVOGLOU E.C., STEIN M., and TOWNE W.W., Control of radioactive pollution of the Animas River, Journal of the Water Pollution Control Federation, 32, 3, 262-287 (1960).

U.S. DEPT. OF HEALTH, EDUCATION AND WELFARE, (1962) "Waste Guide for the Uranium Milling Industry", Public Health Service, Technical Report W62-12.

Chapter 2

ANALYTICAL METHODS

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2.1. METHODS FOR MEASURING ^{226}Ra

For a better understanding of the numerous analytical procedures available for ^{226}Ra determination, let us first look at its decay series in Table 2.1.

If the degree of radioactive equilibrium between radium and its decay products is known, apart from radium any one of the products can be detected in order to determine the radium activity; Thus, a lot of analytical methods for radium exist [Furnica (1969); Weigel (1977b)]. They are based on

- direct identification of radium
- identification of radium decay products
- measurement of gross alpha, gross beta and gross gamma activity of radium together with decay products, or only those of its decay products.

2.1.1. Direct Measurement of Radium Activity

^{226}Ra can be determined directly by alpha and gamma spectrometric methods, which in addition to ^{226}Ra activity also give us the isotopic composition of radium present (isotopes 228, 226, 224 and 223).

In alpha spectrometry, the 4.78 MeV ^{226}Ra alpha peak is analysed [Šebesta et al. (1978); Durrance et al., (in press); Smith, Mercer (1970)].

In gamma spectrometry, the ^{226}Ra 186 KeV peak is used [Durrance et al., (in press); Parks, Pool, Williams (1978); Papastefanou, Charalamous (1978)]. The abundance of this gamma peak is only 4 %, hence one should be aware of possible interference from the ^{235}U 185 KeV peak, with an abundance of 54 % [Powers, Turnage, Kanipe (1980)].

^{226}Ra can also be determined directly when it is isolated from the sample in the form of Ba-Ra sulphate, the sulphate heated to 700°C to remove radon and then radium alpha activity counted on a silver activated zinc sulphide detector [Rao, Borkar, Shah (1970)].

Instead of precipitation, radium can be isolated by electro-plating. The radium containing planchet is heated to remove radon, and radium alpha activity measured on a surface barrier detector [Koide, Bruland (1975)].

2.1.2. Spectrometry of radium decay products

There are several methods of radium determination via identification of its decay products using alpha, beta or gamma spectrometry.

2.1.2.1. Alpha spectrometry

Alpha spectrometry is usually performed for identification of radium decay products in isolated radium-barium coprecipitates [Šebesta et al. (1978); Bland (1980)].

2.1.2.2. Beta spectrometry

For beta spectrometry liquid scintillation counting is performed. The water phase containing ^{226}Ra is mixed with a toluene [Prichard, Gesell, Meyer, draft] or dioxane based [Havlik (1971), Havlik (1973)] liquid scintillator, or only ^{222}Rn is extracted and sorbed in the liquid scintillator and then analysed [Levins, Ryan, Strong (1978); Homma, Murakami (1977); Parks, Tsuboi (1978); Darrall, Richardson, Tyler (1973)]. A special version is time interval liquid scintillation spectrometry [Cross, McBeth (1976a)].

2.1.2.3. Gamma spectrometry

In gamma spectrometry of active samples radium is determined by analysing the ^{214}Bi 1.76 MeV gamma peak [Momeni, Rosenblatt, Jow (1976); Kirchmann et al. (1975); Vernet et al. (1975)], but generally the following peaks are taken into consideration:

- only ^{214}Bi 609 keV [Prestwich, Kenneth (1979)],
- often this one and ^{214}Pb 352 keV [Šebesta et al. (1978); Roessler et al. (1979); Okubo, Furuyama, Sakanove (1979); Kirchmann, Darcheville, Koch (1980); Powers, Turnage, Kanipe (1980); Ekpechi, Van Middlesworth, Cole (1975)],
- sometimes also ^{214}Pb 295 keV [Okubo, Furuyama, Sakanove (1979)], and ^{214}Bi higher energy peaks at 1120 and 1764 keV.

Rarely, preferably in cases of nonequilibrium between radium and its decay products [Thomas et al. (nondated separatum); Thomas, Malatova (1970); Lenger, Thomas (1970)], the whole spectrum of the sample is analysed including also the ^{226}Ra 186 keV peak [Šebesta et al. (1978); Šebesta et al. (1980)].

2.1.3. Gross Counting Methods

Gross activity determination of radium together with its decay products, or those of decay products only is often carried out.

2.1.3.1. Counting on radium precipitate

Radium can be isolated from a dissolved sample by coprecipitation after an appropriate chemical procedure. As the precipitate in most cases a radium-barium sulphate occurs [Schuttelkopf, Kiefer (1979); Yamamoto, Yunoki, Ishida (1977); Asikainen, Kahlos (1977); Asikainen, Kahlos (1979); Asikainen, Kahlos (1980); Levins, Ryan, Strong (1978); Rao, Borkar, Shah (1970); Gregory (1974); Ivan et al. (1976); Martin, Heim, Sigler (1969); Vilenskii (1969); Pietrzak-Flis (1972); Popova, Kyrchanova (1971); Vilenskii, Anikiev (1974); APHA (1974); HASL (updated 1980)], and sometimes also radium-lead sulphate [Baltakmens, (1976); Sladkova et al. (1974); Wlodek, Grzybowska, Bysiek (1970)], and radium-calcium carbonate [Justyn (1973); Justyn, Stanek (1974)].

The alpha activity of the precipitate is usually measured with silver activated zinc sulphide alpha scintillator [HASL (updated 1980); APHA (1974); Smithson (1979)], but some authors also use proportional gas flow counters [APHA (1974); Yamamoto, Yunoki, Ishida (1977); Ivan et al., (1976); Martin, Helm, Sigler (1969); Sladkova et al. (1974)], surface barrier detectors [Smithson (1979)] and Geiger-Müller tubes [Sladkova et al. (1974); Justyn (1973); Justyn, Stanek (1974)].
To improve counting efficiency, the zinc sulphide scintillator can be mixed with the precipitate during precipitation [Kelkar, Joshi (1969)]. For the same reason, gelatine plates with radium-barium sulphate are used according to the sorbemulsion method [Havlik (1971)].

2.1.3.2. Determination by emanometry

(a) Principle

Maybe the most widely used method for ^{226}Ra determination is emanometry [APHA (1974); HASL (updated 1980); Rushing, Garcia, Clark (1964); Smithson (1979)]. According to references available to the author, about a half of all investigations use this method.
The principle of the method is deemanation and isolation of radon ingrown from radium in solution in a known time, and measurement of the activity of radon and its short-lived decay products. The radium containing solution is closed in a vessel, called the radon bubbler, freed of radon by bubbling, stored for 1 - 30 days, depending on the expected radium activity [Sedlaček, Šebesta, Beneš (1980); APHA (1974)], and radon purged from the bubbler into a counting cell.

(b) Measurements

Frequently Rushing type [Rushing, Garcia, Clark (1964)] 15-25 cm^3 glass bubblers are used [Sedlaček, Šebesta, Beneš (1980); APHA (1974); HASL (updated 1980); Smithson (1979)]. In this case the bubbler is simply connected to an evacuated counting cell. A carrier gas is allowed to pass through the solution in the bubbler at a low flow rate (several bubbles per second); it is dried in an ascarite and drierite tube, and collected in the counting cell. In a simplified procedure, the drying tube is not included [Sedlaček, Šebesta, Beneš (1980)]. Due to hydrostatic pressure and tube resistence, the final pressure in the counting cell is usually slightly below atmosphere pressure.
As the carrier gas the following are used;

- helium [Michel, Moore (1980a); Felmlee, Cadigan (1978); Holtzman et al. (1979); Smithson (1979); Miyake, Sugimura, Saruhashi (1980); Haywood et al. (1980); Ku, Lin (1976); Ku et al. (1970)],
- argon [Sladkova et al. (1974); Sedlaček, Šebesta, Beneš (1980)],
- aged nitrogen [Smithson (1979); Holtzman et al. (1979); Scheibel, Porstendorfer, Wicke (1979); El-Daoushy (1978)],
- aged air [Szabo, Tokes, Pall (1973); Levins et al., (1978); Holtzman et al. (1979); Johns et al. (1979)],
- forming gas (15 % H_2, 85 % N_2) [HASL (updated 1980)],
- and PR gas (90 % Ar, 10 % Methane) [Kametani (1975b)].

Helium gives a few percent better counting efficiency than nitrogen [Smithson (1979)].

The alpha activity of radon and its decay products is measured at least 3 to 4 hours after filling the counting cell, when radioactive equilibrium has been reached. For the activity measurements, are used:

- scintillation cells [Rushing, Garcia, Clark (1964); APHA (1974); Sedlaček, Šebesta, Beneš (1980); Michel, Moore (1980a); Johns et al. (1979); Paschoa et al. (1979); Smithson (1979); Miyake, Sugimura, Saruhashi (1980); Powers, Turnage, Kanipe (1980); Szabo, Tokes, Pall (1973)],
- ionization chambers [Ohno, Watanabe (Non-dated report); HASL (updated 1980); El-Daoushy (1978)],
- proportional counters [Kametani (1975); Martin, Helm, Sigler (1969)]
- and liquid scintillation counters [Levins, Ryan, Strong (1978); Homma, Murakami (1977); Darrall, Richardson, Tyler (1973).

Scintillation cells are mostly of Lucas type [Lucas (1957)] available on the market [Smithson (1979)], or produced with some modifications in laboratories using them [Sedlaček, Šebesta, Beneš (1980); Kristan, Kobal (1973); Mastinu (1980); Szy, Urban (1971)]. Instead of glass, cell walls can be made of stainless steel [Scheibel, Porstendorfer, Wicke (1979)] or acrylic plastic [Key et al. (1979)]. The volume of scintillation cells is usually 0.15 to 0.20 dm^3, but there are also smaller [Key et al. (1979)] and larger ones [Mastinu (1980); Szy, Urban (1971)]. The inside walls of the scintillation cells are covered with silver activated zinc sulphide scintillator. The bottom of the cell is transparent and serve as the optical contact with the photomultiplier tube of a low-background scintillation probe.

(c) Low radium concentrations measurements

Apart from conventional pulse height ionization chambers [HASL (updated 1980)], some specially designed chambers are also in use [Sladkova et al. (1974)].

The efficiency of radon transfer from the bubbler into the counting cell is mainly dependent on the volume ratio between the counting cell and the bubbler. Lower radium concentrations require larger sample volumes. In order to keep the small volume Rushing type bubbler, water samples must be concentrated by evaporation, by sorption of radium on a cationic exchange resin or manganese-oxide impregnated acrylic fibers, or by coprecipitation followed by dissolution.

If larger volumes of water or other solubilized samples cannot be avoided, radon from the stored sample is extracted and collected in the counting cell with a carrier gas using radon-transfer apparatus. In this case, a larger volume of carrier gas is used, the expelled gas is purified and dried, radon is isolated from the carrier gas and collected in a previously evaculated counting cell. Depending on the volume and shape of the bubbler, the carrier gas volume ranges from a few [Kobal, Kristan (1972)] to 30 litres [Scheibel, Porstendorfer, Wicke (1979)].

The expelled gas is purified from water by ascarite and drierite [Johns et al. (1979); Miyake, Sugimura, Saruhashi (1980)], concentrated sulphuric acid [Kobal, Kristan (1972)], silica gel and soda lime [Homma, Murakami (1977)], calcium chloride and copper filaments at -78,5°C [Scheibel, Porstendorfer, Wicke (1979)].

Radon is isolated from the carrier gas on a liquid nitrogen cooled trap [Kobal, Kristan (1972); Miyake, Sugimura, Saruhashi (1980); Haywood et al. (1980); Homma, Murakami (1977); HASL (updated 1980)], on a charcoal trap cooled at -78.5°C [Levins, et al., (1978); Kirchmann et al. (1975); Holtzman et al. (1979); Key et al. (1979); Scheibel, Porstendorfer, Wicke (1979)], or on an activated molecular sieve at dry ice temperature [Chung (1976)].

To improve trapping efficiency, fine bronze wool [Key et al. (1979)] or glass beads [Kobal, Kristan (1972)] are used as trap filling. In case of a nitrogen trap, radon expands into the counting cell after warming the trap to room temperature, while desorption from charcoal is caused by heating the trap up to 300 [Key et al. (1979)] or 450°C [Holtzman et al. (1979)].

To assure complete transfer, the radon isolated in a trap can be recondensed in a smaller, additional so-called 'volume reduction trap' and then collected in the counting cell [Key et al. (1979)]. For the same reason, the carrier gas containing the radon is made to circulate in the radon transfer system by means of a dyaphragm type pump [Homma, Murakami (1977)].
The radon transfer system is usually made of glass, but when made of stainless steel tubing it slightly reduces liquid nitrogen consumption [Key et al. (1979)].
To extract radon efficiently from a very large sample volume (55 dm^3), an additional recirculating device speeds up radon release [Broecker, Goddard, Sarmiento (1976)].

Instead of concentrating low activity samples, some authors propose larger and specially shaped scintillation [Mastinu (1980); Szy, Urban (1971)] and ionization cells [Sladkova et al. (1974)].

It is also possible to connect an evacuated scintillation cell to a larger water sample (up to 1 dm^3) and from the activity of radon extracted in this one cell, calculate the total activity of radon present by making an extrapolation [Raghavayya (1968); Kobal, Kristan (1972)].

For liquid scintillation counting, radon is trapped on silica gel at liquid nitrogen temperature [Darrall, Richardson, Tyler (1973)] or at -80°C [Levins, Ryan, Strong (1978)], and then transferred into a toluene-based liquid scintillator at 0°C, or after drying it is directly condensed in the scintillator at liquid nitrogen temperature [Homma, Murakami (1977)]. According to the 'isopiestic' method [Parks, Tsuboi (1978)], the radium containing water sample is directly attached to a vessel with a liquid scintillator, or the sample and solvent can be combined in the scintillation vial [Cooper, Wilks (1981)].

2.1.3.3. Counting of radon after extraction by organic solvent

Instead of deemanation, radon at a known degree of equilibrium with radium present in a water or solubilized sample can be extracted by dissolution in hexane or toluene which is added to the sample and shaken. Gross gamma activity of the solvent is measured after separation [Terning (1970)], or α and β activity is measured via liquid scintillation counting [Gessel, Prichard, Haygood (1978)].

This was a short review of analytical methods for the determination of radium.

2.2. METHODS FOR PREPARING AND ANALYSING SAMPLES

2.2.1. Waters

2.2.1.1. Fresh water

Water samples are taken in the field and transported to an analytical laboratory. The required volume of sample depends on the activity expected and the analytical procedure used. The time interval between sampling and analysing should be as small as possible to prevent radium from adsorbing onto the container walls, as this may result in considerable error [Vdovenko and Dubasov (1975); El-Daoushy (1978)]. This adsorption can be lowered by acidification or by a choice of container material, as illustrated by the work of Šebesta et al, (1980) in Figure 2.1. This shows the percentage adsorption of ^{224}Ra onto the walls of glass and polythylene containerrs as a function of pH. Glass adsorbs more radium than the plastic but, at a pH of 3 or less, adsorption on both types of surface is negligible.

In related work by Šebesta et al. (1980) samples of river water and treated uranium mining waste water were spiked with ^{224}Ra; no significant sorption losses occurred within 4 days. The effect of storing these waters, in plastic bottles, on the distribution of dissolved and suspended ^{226}Ra was also investigated over a period of 53 days; no change was detected in river water samples but the particulate fraction of the waste water increased by 46%, probably due to the delayed formation of $Ba(Ra)SO_4$ particles (the waste waters had been treated with $BaCl_2$ in order to remove the Ra as $Ba(Ra)SO_4$ co-precipitate).

The importance of filtration loss was also examined by the CRP Czechoslovakian group, however the amount of radium retained on the membrane filter was negligible (< 2%) for river water, treated waste water and mine water (1-1000 pg dm^{-3} ^{226}Ra). Beneš et al. (1981) have developed a method of selective dissolution for characterizing the particulate forms of radium in natural and waste waters.

Depending on the radium concentration in a water sample and on the analytical equipment, radium is determined:

- directly, without concentration of radium
- by extracting radon ingrown from radium for a known time in a closed vessel
- by concentrating radium from a larger sample (to several tens of dm^3) and its subsequent determination according to one of the former methods.

(a) Direct determination

Radium at concentrations of several tens of Bq/m^3 can be determined by gamma spectrometric methods using 0.5 dm^3 Marinelli beakers. The sample is sealed for about two weeks and the 295.2, 352.0, and 609.4 keV peaks of ^{214}Pb and ^{214}Bi analysed on a Ge-Li detector [Roessler et al. (1979)].
Frequently, only the ^{214}Bi 609.4 keV peaks is taken into account, but in the case of higher activities, counts under the ^{214}Bi 1.76 MeV peak are enough [Kirchmann et al. (1973)].

When spring water is transferred to a specially shaped spherical vessel and gamma analysis is carried out, counting for 180 minutes, concentrations down to a few tens of Bq/m^3 can be determined [Bizollon, Moret, Molgatini (1971)].
Using larger (1.5 dm^3) and specially constructed scintillation cells, a sensitivity of 1.8 [Szy, Urban (1971)] or 3.7 Bq/m^3 [Mastinu (1980)] can be reached.
Larger ionization chambers (2.3 dm^3) are also sensitive enough to measure 5.5 mBq of radium in water without reconcentration [Sladkova et al. (1974)].
Expelling radon from a solution into a gas proportional counter can be a suitable method for activities above 50 mBq [Kametani (1975b)].

(b) Determination by transferring radon in an appropriate counting cell

For lower concentrations, the Rushing type bubbler is too small to contain enough activity to be detected by ordinary counters. In such cases larger bubblers (0.5 to 0.8 dm^3) are used and the radon, extracted by a carrier gas, is transferred to a counting cell by one of the procedures mentioned above [Michel, Moore (1980a)], Paschoa (1977); Paschoa et al. (1979); Scheibel, Porstendorfer, Wicke (1979); Miyake, Sugimura, Saruhashi (1980)].

(c) Determination after concentrating radium

In the majority of cases of environmental water samples, usually having low radium concentrations, radium is first concentrated and then determined. For concentrating radium the following procedures are used:

- evaporation
- coprecipitation
- sorption on ion exchange resins
- sorption on manganese-impregnated acrylic fibres

(i) Evaporation
The sample volume can be simply reduced by evaporation [Kirchmann et al. (1975); Holtzman et al. (1979); Rao, Borkar, Shah (1970); Haywood et al. (1980); Havlik (1971); Havlik (1967); Zettwoog (1978); Saumande, Reix, Beck (1973)] to a final volume suitable for a direct emanation into the counting cell.

(ii) Coprecipitation
The most widely used method for concentrating radium is coprecipitation on barium sulphate [De Jesus, Malan, Basson (1978); Johns et al. (1979); Smithson (1979); Rao, Borkar, Shah (1970); Felmlee, Cadigan (1978); HASL (updated 1980); Rushing, Garcia, Clark (1964)], lead sulphate [Olteanu (1975)], barium chromate [HASL (updated 1980)], calcium carbonate [Kurosawa (1978); Justyn (1973); Justyn, Stanek (1974)] or ternary phosphomolybdate in polyethylene glycol [Sedlaček, Šebesta, Beneš (1980)]. An appropriate carrier should be added to obtain the radiochemical yield. After washing and appropriate chemical purification, the precipitate is either stored for a known time and measured by gamma spectrometry [Šebesta et al. (1978)] or by alpha counting [Schuttelkopf, Kiefer (1979); Asikainen, Kahlos (1977); Asikainen, Kahlos (1979); Asikainen, Kahlos (1980); Smithson (1979); Martin, Helm, Sigler (1969); Vilenskii (1969); Kelkar, Joshi (1969); Wlodek, Grzybowska, Bysiek (1970); Khademi, Mahdavi (1974); Sladkova et al. (1974); Vilenskii, Anikiev (1974);

APHA (1974); HASL (updated 1980)], or dissolved, transferred to a Rushing type bubbler, and radium determined by emanation [Sedlaček, Šebesta, Beneš (1980); Kurosawa (1978); Felmlee, Cadigan (1978); Johns et al. (1979); Smithson (1979); Olteanu (1975); APHA (1974); HASL (updated 1980); Rushing, Garcia, Clark (1964)] as described in previous chapters.

(iii) Sorption on ion exchange resins
Radium from a 20 dm^3 (or larger) water sample can be concentrated by sorption on a cationic exchange resin. The resin is stored for a desired time and then bubbled with a carrier gas. The ingrown radon is then transferred to a counting cell and measured [Kobal et al. (1974)].

(iv) Sorption on manganese-impregnated acrylic fibres
In fresh water radium can also be successfully concentrated by sorption on manganese impregnated acrylic fibres [Bland (1980)], though this method was developed [Moore, Reid (1973)] and is widely used for analysing sea water samples. Radium is removed from the fibre by boiling in concentrated hydrochloric acid and the extracted solution transferred to a Rushing type bubbler.

2.2.1.2. Sea water

In the case of sea water, the sample volume ranges from 20 [Reid (1979); Ku, Lin (1976); Olteanu (1975)] up to 1000 dm^3 [Okubo, Furuyama, Sakanove (1979)].

Generally, methods for ^{226}Ra determination in sea water can be devided into three types.

(a) Radon extraction

Radon extraction from water and measurement of its alpha activity [Michel, Moore (1980b)], Chung (1976); Ku, Lin (1976); Broecker, Goddard, Sarmiento (1976); Kelkar, Joshi (1969)]. In order to speed up radon extraction, an auxiliary bubbling device can be added to the bubbling container [Broecker, Goddard, Sarmiento (1976)], and for more efficient isolation of radon from the expelled gas, an activated charcoal molecular sieve is used [Chung (1976)].

(b) Radium concentration

Radium is concentrated from a larger volume of sea water by adsorption on manganese-oxide impregnated acrylic fibres [Key et al. (1979), Moore, Reid (1973); Reid (1979)]; then the fibres are leached with acid and the radium containing solution transferred to a bubbler and radium determined emanometrically.

(c) Radium extraction

Radium is isolated from sea water by chemical procedures. If radium-barium coprecipitate is analysed on a Ge-Li detector, radium can be determined from the 295 and 352 keV peaks of ^{214}Pb and a 609 keV peak of ^{214}Bi [Okubo, Furuyama, Sakanove (1979)].
By a more complex chemical treatment [Koide, Bruland (1975)], radium can be isolated in a form suitable for electroplating. The planchet with

radium is ignited (in order to remove radon) and radium is alpha counted on a pulse height analyser connected to a surface barrier detector.

2.2.2. Soil, Sediments, Ore, Tailings

These samples can be analysed either in their solid form or they are solubilized and radium determined by one of the previously mentioned methods, or a selective dissolution can be made [Benes et al. (1981)].

2.2.2.1. Solid samples

The radium content can be evaluated from a gross beta count of a solid sample on a low level beta counter [Paul, Londhe, Pillai (1980)].

For a crude approximation, a solid sample is placed in distilled water for a time, and the radium in the water determined [Emerson, Hesslein (1973)]. This procedure is also used to determine only the activity of radium adsorbed on sediment particles [Key et al. (1979); Rao, Borkar, Shah (1970)].

Using NaI or Ge(Li) detectors in gamma spectrometry, radium can be determined in intact solid samples [Roessler et al. (1979); Schuttelkopf, Kiefer (1979); Durrance et al. (In press); Haywood et al. (1980); Yasstrebov (1973); Vernet et al. (1975); Baltakmens, (1976); Dobbs, Matthews (1976); Miller, Fix, Bramson (1980); Kirchmann, Darcheville, Koch (1980)]. In anticoincident gamma spectrometry, the interference of ^{40}K can be eliminated [Prestwich, Kenneth (1979)]. Samples are sealed and stored until radioactive equilibrium between radium and its decay products is reached. To prevent radon from possibly escaping from sealed bags, powdered samples can be mixed with charcoal which adsorbs it [Kirchmann, Darcheville, Kock (1980)].

2.2.2.2. Dissolved samples

More often solid samples are solubilized [HASL (updated 1980); Rushing, Garcia, Clark (1964)]. Depending on the chemical composition of the sample this process can be simple, but in some cases it is very complex and time-consuming. Special care should be paid to the removal of silicon, which, when present, decreases the recovery yield of radium [Zimmerman, Armstrong (1975); Terning (1970); Kirchmann et al. (1973)].

In the dissolved sample, radium can be determined by:

(a) Deemanation technique [Ryan, Levins (1980); Ohno, Watanabe (Non-dated report); Kirchmann et al. (1975); Iyengar (1980); Fisenne et al. (1979); Fisenne et al. (1980); Johns et al. (1979); Borole, Somoyalulu (1977); Kametani (1975a); Martin, Helm, Sigler (1969); Popova, Kyrchanova (1971); El-Daoushy (1978); Justyn (1973); Justyn, Stanek (1974); Rushing, Garcia, Clark (1964)], extracting radon by bubbling and transferring it to a counter cell.

(b) Radium is electroplated on a planchet, the planchet ignited to remove radon and then the gross alpha activity of the planchet is counted or alpha spectrometric analysis based on 4.78 KeV radium peak performed [Koide, Bruland (1975)].

(c) Coprecipitation of radium in the form of radium-barium sulphate followed by gross alpha measurement [Baltakmens, (1976); Rao, Borkar, Shah (1970); Yamamoto, Yunoki, Ishida (1977)] or alpha spectrometry [Zimmerman, Armstrong (1975)] of the precipitate.

(d) Extraction of radon from the radium bearing solution by hexane and subsequent measurement of the gamma activity of the radon and its daughters [Terning (1970)].

(e) Sorbemulsion method using gelatine plates with radium-barium sulphate counted on an alpha scintillation counter [Vlček (1962)].

2.2.3. Food

2.2.3.1. Liquid food

^{226}Ra content in milk can be determined by a direct deemanation of radon from the milk [Kirchmann et al. (1973); Kirchmann et al. (1972)], or milk is firstly evaporated, dried and ashed, and then the ash can be analysed by gamma spectrometry [Schuttelkopf, Kiefer (1979)]. Alternatively, it is firstly solubilized and radium determined by deamanation of radon [Khademi, Mahdavi (1974)] or by electroplating radon daughters followed by alpha scintillation measurement [Treuelle (1977)].

2.2.3.2. Solid food

(a) Techniques involving ashing
Food and vegetables samples are dried and ashed. The ash is treated as follows:
  (i) The ash is analysed by gamma spectrometry using a Ge(Li) detector [Schuttelkopf, Kiefer (1979)].
  (ii) The ash is dissolved and radium determined by
    - coprecipitation with barium sulphate and subsequent measurement of alpha activity of the precipitate using silver activated zinc sulphide [Smithson (1979)] or a low background gas-flow proportional counter [Ivan et al., (1976)]
    - electroplating radon daughters from the solution followed by alpha scintillation counting of the planchet [Treuelle (1977)].

(b) Techniques involving pulverization
Plant samples are dried and pulverized.
  (i) Ready pulverized samples can be analysed by gamma spectrometry [Miller, Fix, Bramson (1980)], or samples are first ashed and gamma spectrometry of the ash carried out [Schuttelkopf, Kiefer (1979)].
  (ii) The ash is dissolved and radium determined by
    - emanometry [Holtzman et al. (1979); Bloch et al. (1980); Popova, Kyrchanova (1974)]
    - alpha spectrometry of the electroplated radium [Smithson (1979)]
    - sorbemulsion method with alpha scintillation counting radium-barium sulphate gelatine [Havlik (1971)]
    - alpha scintillation counting of the radium-barium oprecipitate [Smithson (1979)].

2.2.4. Animal Materials

2.2.4.1. Bones

(a) ^{226}Radium content of bone samples (bones, teeth, fossils, corals) is often obtained by nondestructive gamma spectrometry of powdered samples [Momeni, Rosenblatt, Jow (1976); Komura, Sakanove, Konishi (1978); Charalambous, Papastefanou (1977); Papastefanou, Charalambous (1978)].

(b) If samples are ashed and dissolved, radium is determined by
  - emanometry with [HASL (updated 1980)] or without coprecipitation with barium sulphate [Kirchmann et al. (1975)] or
  - alpha scintillation counting of radium-barium sulphate [Gregory (1974)].

(c) Radium retained in animal bones can also be determined by whole body gamma spectrometry [Momeni, Rosenblatt, Jow (1976); Parks, Pool, Williams (1978)].

2.2.4.2. Urine, blood

(a) Urine samples are filtered and chemically treated in order to obtain a clear solution in which radium is determined by a direct emanometry [Lucas, Marschal, Barrer (1970)], or radium is firstly extracted by barium sulphate coprecipitation [HASL (updated 1980)]; Smith, Mercer (1970)].

(b) Also liquid scintillation technique can be successfully used for determination of the radium content of urine [Parks, Tsuboi (1978)].

(c) Similar procedures can be used for radium determination in blood [Lucas, Marschal, Barrer (1970)].

2.2.4.3. Excreta

Excreta samples are first dried and ashed, the ash is dissolved and radium determined by

(a) Emanometry [Lucas, Marschal, Barrer (1970)] or

(b) Coprecipitation of radium-barium sulphate followed by
  - gamma spectrometric analysis of the precipitate [Vanderborght, Colard, Boulenger (1972)],
  - dissolution of the precipitate and emanometric determination [HASL (updated 1980); Smith, Mercer (1970)].

2.2.4.4. Whole body counting

High activities of ^{226}Ra retained in the animal and human body by ingestion can also be measured by gamma spectrometry using a whole body counting system [Lucas, Marschal, Barrer (1970)]; Vanderborght, Colard, Boulenger (1972); Thomas et al. (nondated separatum); Lenger, Thomas (1970)].

2.3. INTERPRETATION OF RESULTS

2.3.1. Components of the Random Precision Error

A quantitative estimate of the uncertainty associated with any radiochemical analysis is necessary in three important applications:

- comparing monitoring data with prescribed standards,
- intercomparison of different methods of analysis, and
- estimating the lower limit of determination in a given method.

Handbooks on radiochemistry outline the methods involved in estimating this uncertainty and Donn and Wolke (1977) with the correction of Barry (1979) have provided the means of determining the sample size required to make correct decisions on low-level monitoring data. However these methods all assume that the error is due only to a simple, random, radioactive decay process, approximated by the Poisson distribution, and for two reasons this is invalid for common methods of radium analysis.

Firstly, the time intervals commonly used in radon counting are long compared to the half-life of ^{218}Po (3 minutes) and ^{214}Po (1.64×10^{-4} seconds, Table 2.1) and this means that, for example, each ^{222}Rn decay will almost certainly be followed by a ^{218}Po decay within 15-20 minutes, and so the total number of counts recorded are not all independent, random events. Lucas and Woodward (1964) examined this problem theoretically and derived a correction factor as follows:

$$\sigma = \sqrt{JN}$$

where σ = standard deviation of N counting events. They found that J varies between 1 and 2.9 depending on the counting interval and the counting efficiency, and they provided Tables and Figures that evaluate J for a range of conditions. Sarmiento et al. (1976) independently examined this problem and introduced an approximation to simplify calculation. Key (1977) compared the two methods and concluded that the Sarmiento approximation was useful for counting times in excess of 300 minutes, otherwise the Lucas method was preferred. Jonassen and Clements (1974) used the simple expedient of estimating the counts due to ^{222}Rn alone and taking the square root of that as the standard deviation. They then obtained some experimental values for the standard deviation of radon-in-air measurements and found that these were consistently higher than the simple Poisson estimate based on total counts (3.9% coefficient of variation), and on average (4.7%), were below the estimate based on ^{222}Rn activity alone (6.4%). It is unfortunate that the theoretical works of Lucas and Woodward (1964) and Sarmiento et al. (1976) were not also compared with experimental data.

The second reason why the simple Poisson model is inadequate is that error sources other than radioactive decay always influence radiochemical analysis and thus should be included in the estimate of precision error. Sarmiento et al. (1976) recognized this and included empirical terms in their model for the variance of the background, the blank, the volumetric measurement and the calibration; in a typical sample of seawater, in which the activity of ^{222}Rn was 1 mBq kg^{-1} and the coefficient of variation was 6.3%, they found the following contributions to the total variance:

Calibration	58.4%
Radon decay	32.1%
Blank	7.4%
Background	1.4%
Volume	0.7%

The Australian group [Williams, O'Brien, Mears (1981)] also approached error estimation from this point of view in studying the routine performance of their method for ^{226}Ra analysis in water using a charcoal radon trap and plastic scintillation cell. Their findings were as follows:

- The empirical precision error ranged from 7% (coefficient of variation) at 1 mBq to 4% at 100 Bq, and this was approximated by the simple Poisson error model only at activities below 100 mBq.
- The background of the scintillation cells did not increase over a period of 1.5 years, contrary to some findings elsewhere [Powers, Turnage, Kanipe (1980)].
- The system carried over about 0.35% of the radon from one sample to another, which could lead to significant error if low activity samples are analysed directly following high activity samples without flushing in between.
- A large component of the error (7% coefficient of variation) was due to calibration, and was normally distributed (i.e. not due to counting error).
- Gross errors were sufficiently common to require analysis of all samples at least in duplicate, to ensure 90% probability that a given result falls within a 95% confidence interval of the true value.
- As the Poisson error model failed to explain the observed errors, a combined Poisson and Normal model was derived which did explain what was observed. This model predicted that, with 200 counting events and/or a counting time of 200 minutes, the precision error will range between 7% and 12% (coefficient of variation) for sample activities greater than 10 mBq and background less than 0.5 cpm (min^{-1}). For lower activities, fewer counting events, shorter counting times or higher backgrounds,
  the precision error becomes much larger. The lower limit of determination was estimated by an iterative method and was found to be mainly dependent on counting error; long counting times and low backgrounds giving an increasingly lower limit, while variation in blank errors and calibration errors had little effect; the limit was $\sim$ 1 mBq for a counting time of 200 minutes and background of 0.05 cpm (min^{-1}).

Because the errors found by Williams, O'Brien, Mears (1981) were larger than those found or predicted by Lucas he pointed out their neglect of his theoretical "J" correction and of his specification of metal rather than plastic scintillation cells (Lucas, 1982). In reply, Williams and O'Brien (1982) defended the performance of plastic cells and pointed out that the existence of the non-counting errors can nullify the usefulness of the "J" correction, using the intercomparison data [Williams (1981)] as a prime example.

There is an obvious need for a synthesis of these different points of view and in the light of the present discussion, we recommend the use of the Poisson-Normal model of Williams, O'Brien, Mears (1981), but with a correction included to account for the lack of independence in the ^{222}Rn-daughter decay; to this latter end we recommend a comparison between the methods of Lucas and Woodward (1964), Sarmiento et al. (1976) and Jonassen and Clements (1974) based on adequate experimental data from ^{226}Ra analysis of water.

2.3.2. Inter-Laboratory Comparison

As part of the IAEA Coordinated Research Program, an intercomparison of ^{226}Ra analysis of water was carried out and is reported in Williams (1981). Eight countries participated in analysing three replicates of two water samples (0.17 Bq L^{-1} and 22 Bq L^{-1}). Four countries used methods which involved pre-concentration of radium followed by direct de-emanation of radon into a scintillation cell [denoted "Method C", e.g. Rushing, Garcia, Clark (1964); Sedlaček, Šebesta, Beneš (1980)], and four countries used methods which involved direct de-emanation of radon from an unprocessed sample, with [Lucas (1957); Kobal, Kristan (1972)], or without a radon trap intervening before transfer to a scintillation cell (denoted method D).

The result of the intercomparison was that the C methods were more precise than the D methods. The C method results all clustered within the range of the within-laboratories variation (i.e. there was not greater variation between laboratories than within laboratories); the standard deviations were 10% for the 0.17 Bq dm^{-1} sample and 6% for the 22 Bq dm^{-1} sample. The D method however contained extra random variation that could only be explained by a standard deviation of 12% for both samples.

Other intercomparisons of ^{226}Ra analysis in water have been carried out. The U.S. Environmental Protection Agency has reported intercomparison data [Jarvis, Smiecinski, Easterly (1976); Shawver (1980)] using the Rushing method [Johns et al. (1979)]. In both studies 80% of laboratories fell within the $\pm$ 3 σ range of the known value for ^{226}Ra; the precision errors were, respectively, 19-20% and 17-25% coefficient of variation.

An intercomparison of ^{226}Ra analysis in sea water, under the GEOSECS program, has also been reported by Chung et al. (1974); Chung (1976); Broecker, Goddard, Sarmiento (1976); and Ku, Lin (1976). A large number of samples were analysed, not necessarily from an homogenised stock, and the data were not thoroughly analysed. However, a typical result was that of Table 2 in Chung et al. (1974) where 6 samples were analysed by each of three laboratories; the average concentration of ^{226}Ra was 1 mBq kg^{-1} and the pooled within-laboratory precision error (based on replicate analysis of each sample) was 9% coefficient of variation. The expected precision error due to radioactive decay in 20 mBq of ^{226}Ra (20 dm^3 samples were used) for a 200 minute counting time would be in the range of 9-11%. A systematic error was evident between the laboratories but it did not at any time exceed $\pm$ 2 σ based on the within-laboratory precision error of 9% (the previously mentioned studies used a $\pm$ 3 σ definition of agreement). Thus all three laboratories were able to maintain their accuracy well within the limits of their precision.

The seawater intercomparison therefore provided by far the best results with a precision error no larger than that attributable to radioactive decay and a range of agreement spanning a factor of 1.4 (± 2 x 9%). In contrast the U.S.E.P.A. studies found a range of agreement of a factor of 4 (± 3 x 20%) and the present IAEA study found a range of agreement of a factor of 2 (± 3 x 12%). It is not possible within the scope of this document to examine the reasons behind this large variation in performance, however it is clear that good agreement can be achieved, and so we recommend that a between-laboratory random error of < 10% is a realistic goal and an error as high as 20% should not be accepted.

2.4. CONCLUSIONS AND RECOMMENDATIONS

As was shown in the previous sections, we may conclude that each method can be appropriate for radium determination provided that it is carried out skillfully and that all precautionary measures are taken into consideration.

Direct nondestructive methods are preferred, but radium concentration in environmental samples is seldom high enough to allow it to be applied. These methods can be used for analysing uranium ores, tailings, water from tailing ponds, some sediments and other more active samples.

In the majority of cases, radium should be firstly concentrated (and/or isolated) from the sample and then determined according to one of the methods described already. For water samples, evaporation, co-precipitation and adsorption are used for concentration. Each procedure has its advantages and disadvantages. Most frequently barium is used for coprecipitation, but calcium-barium precipitate is more convenient for filtration and centrifugation [Kurosawa (1978)]. Coprecipitation with the ternary complex of calcium phosphomolybdate and polyethylene glycol facilitates dissolution of radium [Sedlaček, Šebesta, Beneš (1980)].

Radium once dissolved (water samples or solutions after preconcentration or after isolation from solid samples) can be determined by direct emanation measuring radon gas, or by reprecipitation and measurement of the activity of the precipitate.
Emanation is preferred because it is specific for ^{222}Rn gas, and measuring its own and its daughters' alpha activity enables us to determine ^{226}Ra in the presence of even high activities of ^{223}Ra and ^{224}Ra. It is much less sensitive to this interference than alpha-counting of the precipitate [Smithson (1979); Rushing, Garcia, Clark (1964)].

A promising new method of ^{226}Ra analysis is low-background liquid scintillation α -counting [McDowell (1980] using pulse shape as well as pulse height discrimination, and utilizing the high solubility of radon in organic solvents such as toluene. We recommend further development of these concepts.

But the main point on which one can decide which method to use is the nature of the sample (water, soil, ore, biological material, etc.) and the radium concentration in it. Thus the choice lies with the lower limit of detection of a method - LLD [HASL (updated 1980)].

With gamma spectrometry of water samples (0.5 dm^3, 8 h counting) an LLD of 1.2 to 2.6 $kBqm^{-3}$ is obtained (depending on the efficiency of Ge-Li detector) while the emanation method gives (200 min count) 1.5 Bqm^{-3} [Powers, Turnage, Kanipe (1980)]. For soil both methods have an LLD of the same order of magnitude, namely 0.7 Bq kg^{-1} with emanation and from 1.1 to 2.6 Bq kg^{-1} with gamma spectrometry [ibidem]. Certainly, the LLD is dependent on the measuring equipment as well as on counting times and background [Šebesta et al. (1980)]. Thus, according to other sources, LLD in emanation method is 3.7 Bqm^{-3} for 100 min counting [Smithson (1979)], from 1.1 to 1.9 Bqm^{-3} [APHA (1974)], 3 m Bq for 400 min and 1.7 m Bq for 1000 min count [HASL (updated 1980)].
Determination of radium by measuring alpha activity of the precipitate from a 0.5 dm^3 water sample has (for a 100 min count) an LLD of 3.7 Bqm^{-3} [Smithson (1979)], but for a 400 min count it is 3 mBq, and for 1000 min count 1.7 mBq [HASL (updated 1980)].
Where preconcentration of radium is carried out, the LLD can be lowered by taking larger sample volumes.

The analytical procedure should be also chosen in accordance with the aims of the investigation, namely which forms of radium, for instance in water, are to be determined: soluble radium, insoluble radium, radium adsorbed on solid particulates, weakly adsorbed radium, total radium, and so forth [Šebesta et al. (1978); Šebesta et al. (1980) Beneš et al. (1981)]. To this aim, it is not enough to take care of the appropriate procedures and equipment, but special precautions should also be undertaken in sample collection, treatment and storage before analysis [Šebesta et al. (1980)].

In order to be able to compare the results of radium determinations among different publications, authors should treat their results statistically and give details of the procedure used.
Interlaboratory comparison has shown that it is possible for laboratories to operate within the limits of error determined by radioactive decay (2-10% coefficient of variation) and thus we recommend that this be set as a goal of quality control.
Some of the existing data on ^{226}Ra in the international literature may be subject to error beyond that attributable to radioactive decay and ranging between 12-20% coefficient of variation; this should be taken into account when comparing such results.

In gross counting methods (i.e. ^{226}Ra and/or ^{222}Rn plus daughters) the precision error should not be estimated from the simple Poisson model because ^{222}Rn daughter decay is not independent of ^{222}Rn decay, and because non-Poisson errors also occur in sample handling and machine operation. An optimum error model has yet to be devised and we recommend a synthesis of the Poisson-Normal model with the simplest decay correction that fits the experimental data. Once such a satisfactory error model is devised it should be used to estimate the precision of individual sample analyses, to estimate the limit of determination of the method, and to test monitoring data against prescribed limits.

Gross error is common in radiochemical analysis; we recommend duplicate analysis of important samples and rejection of outliers (especially if the frequency of gross error exceeds 5% in your laboratory).

Table 2.1

Decay modes and energies of ^{226}Ra and its main daughter products, in order [from Weast (1978)]

Isotope	Half-life	Decay mode	Particle energy (MeV)	Particle intensity %	Gamma energy (MeV)	Gamma intensity %
^{226}Ra	1600 a(*)	α	4.781	94.5	0.186	100.
			4.598	5.5	0.260	0.29
			4.340	0.006	0.420	0.021
			4.194	0.0009	0.450	0.009
			4.160	0.0003	0.610	0.033
^{222}Rn	3.823 d	α	5.486	100.	0.510	0.07
			4.984	0.08		
			4.824	0.0005		
^{218}Po	3.05 min	α	6.002	99.9		
			5.181	0.0011		
		β-		0.019		
^{214}Pb	26.8 min	β-	0.59	6.	0.053	
			0.65		0.196	
			1.03		0.206	
					0.242	3.7
					0.259	
					0.272	
					0.275	
					0.279	
					0.295	
					0.352	36.
					0.481	
					0.534	
					0.549	
					0.777	
^{214}Bi	19.7 min	β-	0.82	2.	0.063	
			1.06	8.	0.191	
			1.14	5.	0.450	1.
			1.41	8.	0.609	47.
			1.50	19.	0.666	2.
			1.51	19.	0.703	0.8
			1.88	10.	0.721	0.7
			1.98	2.	0.769	5.3
			2.65	5.	0.787	1.2
			3.26	19.	0.806	1.5
		α	4.941	0.25	0.821	
		(0.04%)	5.023	0.21	0.825	
			5.184	0.6	0.874	0.4
			5.268	5.8	0.935	3.3
			5.448	53.9	0.960	0.5
			5.512	39.2	1.050	0.5

(*) 1617a [Weigel (1977a)]

Table 2.1 (cont.)

Isotope	Half-life	Decay mode	Particle energy (MeV)	Particle intensity %	Gamma energy (MeV)	Gamma intensity %
^{214}Bi					1.120	16.
					1.155	1.8
					1.207	0.6
					1.238	6.0
					1.281	1.7
					1.379	4.8
					1.39-1.40	4.
					1.416	
					1.509	2.4
					1.541	0.8
					1.583	0.9
					1.600	0.6
					1.661	1.2
					1.681	0.2
					1.728	3.2
					1.764	17.
					1.836	0.3
					1.848	2.3
					1.877	0.2
					1.897	0.3
					2.017	0.07
					2.090	
					2.117	1.3
					2.162	
					2.204	6.
					2.435	2.
					2.700	0.04
					2.770	0.04
					2.890	0.04
					2.990	0.04
					3.070	0.04
^{214}Po	1.64 x 10^{-4}s	α	7.687	99.	0.800	0.014
			6.905	0.01		
			+ long range α			
^{210}Pb	21 a	β-	0.015	81.	0.047	4.1
			0.061	19.		
		α	3.72	1.7×10^{-6}		
^{210}Bi	5.01 d	β-	1.160	99.		
		α	4.654	0.00013		
			4.691			

Table 2.1 (cont.)

Isotope	Half-life	Decay mode	Particle energy (MeV)	Particle intensity %	Gamma energy (MeV)	Gamma intensity %
^{210}Po	138.4 d	α	5.305		0.803	0.0012
^{206}Pb	stable					

Note: ^{218}At, ^{218}Rn, ^{210}Tl and ^{206}Tl also occur in the decay chain but with yields ≦ 0.08%.

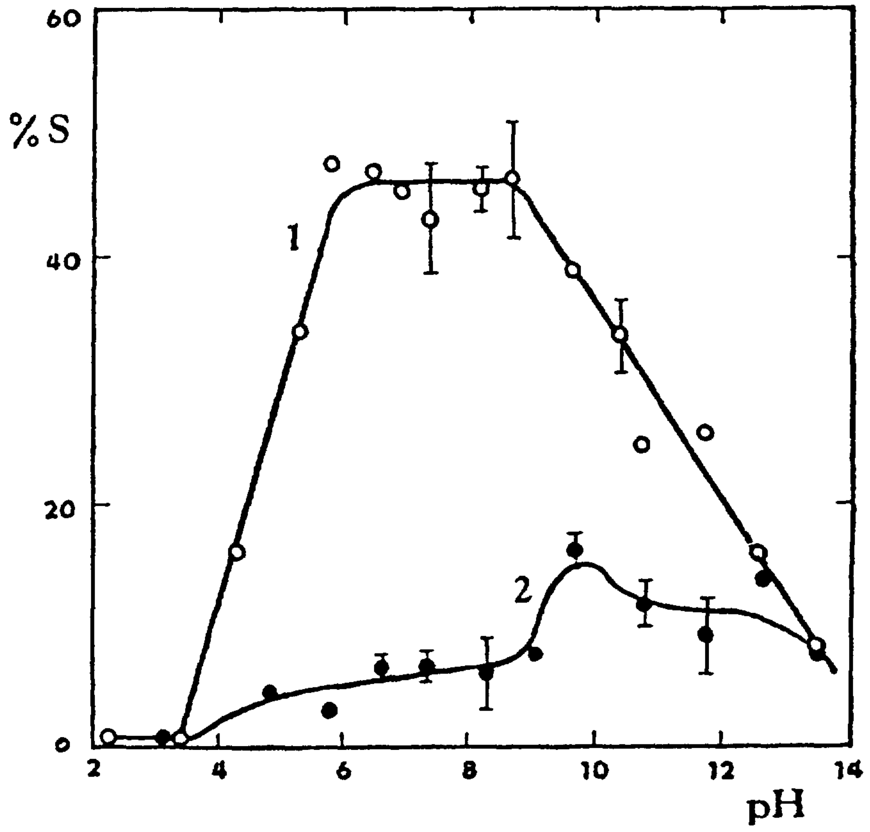

Fig.2.1 Adsorption of radium on glass (1) and polyethylene (2) as a function of the pH value of the solution. Initial concentration of ^{224}Ra 20 pg L^{-1}, ionic strength of the solution 0.01 (as NaCl); pH adjusted with HCl and NaOH; data points represent means of 2-6 replicates, bars represent standard deviations from 4 replicates. Data of Šebesta et al (1980).

REFERENCES

APHA
"Standard Methods for the examination of water and wastewater", American Public Health Association, Washington D.C., 13th Ed., (1974).

ASIKAINEN M., KAHLOS H.
"Pohja-ja Dintavesien Luonnollinen Radioaktiivisuus Suomessa". Institute of Radiation Protection, Helsinki, Finland, Raporrtti STL-A24 (1977).

ASIKAINEN M., KAHLOS H.
"Anomalously high concentrations of uranium, radium and radon in water from drilled wells in the Helsinki region".
Geochem. Cosmochim. Acta 43, 1681 (1979).

ASIKAINEN M., KAHLOS H.
"Natural radioactivity of drinking water in Finland",
Health Phys. 39, 77 (1980).

BALTAKMENS T.
Uranium-238 and Radium-226 equilibrium and thorium: uranium ratio in New Zealand soil - their relationship to iron and potassium content
New Zealand J. Sci. 19, 375 (1976).

BARRY B.J.
Comments on "The statistical interpretation of counting data from measurements of low-level radioactivity" by J.J. Donn and R.L. Wolke,
Health Phys. 36, 208-9 (1979).

BENEŠ P., SEDLAČEK J., ŠEBESTA F., ŠANDRIK R. and JOHN J.
"Method of selective dissolution for characterization of particulate forms of radium and barium in natural and waste waters".
Water Res. 15, 1299-1304 (1981).

BIZOLLON C.A., MORET R., MOLGATINI J.P.
"Methode de mesure directe des teneurs en radium et en radon des eaux de source à l'aide de la spectrométrie gamma".
Ann. Phys. Biol. Med. 5, (1971) 45.

BLAND C.J.
"Measurements of radium in water using impregnated fibres".
Natural Radiation Environment III (Proc. Symp., Houston, Texas, USA, 1978), CONF-780422, 1, 458 (published 1980).

BLOCH E.W., DESAI N., ROESSLER C.E., KAUTZ R.S.
"Determination of radon flux from complex media: virgin and reclaimed lands in Florida Phosphate Region".
Natural Radiation Environment III, (Proc. Symp., Houston, Texas, USA, 1978) CONF-780422, 2, 1673 (publ. 1980).

BOROLE D.V., SOMOYALULU B.L.K.
"Radium and lead-210 in marine barite".
Marine Chem. 5, 291 (1977).

BROECKER W.S., GODDARD J., SARMIENTO J.L.
"The distribution of ^{226}Ra in the Atlantic Ocean".
Earth Planet. Sci. Lett. 32, 220 (1976).

CHARALAMBOUS S., PAPASTEFANOU C.
"On the radioactivity of fossil bones".
Nucl. Instrum. Methods 142, 581 (1977).

CHUNG Y., CRAIG H., KU T.L., GODDARD J., BROECKER W.S.
"Radium-226 measurements from three Geosecs intercalibration stations".
Earth Planet. Sci. Lett. 23, (1), 116 (1974).

CHUNG Y.C.
"A deep ^{226}Ra maximum in the Northeast Pacific".
Earth Planet. Sci. Lett. 32, 249 (1976).

COOPER M.B., WILKS, M.T.
An analytical method for radium (^{226}Ra) in environmental samples by the use of liquid scintillation counting.
Australian Radiation Laboratory, Yallambie, ARL/TR040 (1981).

CROSS P., McBETH G.W.
"Absolute determination of trace quantities of the ^{226}Ra series by time interval analysis".
Nucl. Instrum. Methods 137, 135 (1976).

CROSS P., McBETH G.W.
"Liquid scintillation alpha particle assay with energy and pulse shape discrimination",
Health Phys. 30, 303 (1976).

DARRALL K.G., RICHARDSON P.J., TYLER J.F.C.
"An emanation method for determining radium using liquid scintillation counting". Analyst 98, 610 (1973).

DAY P.R.
"Report of the Committee on Physical Analyses, 1954-55".
Soil Science Society of America, Soil Sci. Soc. Proc. 20, 167-169 (1956).

DE JESUS A.S.M., MALAN J.J., BASSON J.K.
"Movement of radium from South African gold/uranium mine dumps into the aqueous environment".
Report at the IAEA Third Coordination Meeting of "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers", Las Vegas, Nevada, USA, October 1978.

DOBBS J.E., MATTHEWS K.M.
"A survey of naturally occurring radionuclide concentration in New Zealand soils".
New Zealand J.Sci. 19, 243 (1976).

DONN J.J., WOLKE R.L.
"The statistical interpretation of counting data from measurements of low level radioactivity",
Health Phys. 32, 1-14 (1977).

DURRANCE E.M., MEADS R.E., BRINDLEY R.K., STARK A.G.W.
"Radioactive disequilibrium in uranium-bearing nodules from the New Red Sandstone (Permian-Triassic) of Budlegh Salterton, Devari".
(In press).

EKPECHI O.L.V., VAN MIDDLESWORTH L., COLE G.
"Natural ^{226}Ra and ^{228}Th in thyroids of cattle from Nigeria, W. Africa".
Int.J.Nucl.Med.Biol. 2, 31 (1975).

EL-DAOUSHY M.F.A.F.
"The determination of Pb-210 and Ra-226 in lake sediments and dating applications".
Upsala University Institute of Physics,
Report UUIP-979 (1978).

EMERSON S., HESSLEIN R.
"Distribution and uptake of artificially introduced radium-226 in a small lake".
J. Fisheries Res. Board Canada 30, 10, 1485 (1973).

EPA
"Environmental radioactivity laboratory intercomparison studies program 1978-79 Environmental Monitoring and Support Laboratory, Las Vegas, USA",
Report EPA-600/4-78-032 (1978).

FELMLEE J.K., CADIGAN R.A.
"Radium and uranium data of mineral springs in eight Western States".
U.S. Department of the Interior, Geological Survey, Open-File Report 78-561 (1978).

FISENNE I.M., WELFORD G.A., PERRY P., BAIRD R., KELLER H.W.
"Distribution of ^{234}U, ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po in soil".
Environment Int. 1 5 245 (1979).

FISENNE I.M. PERRY P.M., KELLER H.W.
"Wet and dry deposition of ^{226}radium, ^{210}lead and stable lead in an urban environment".
Environmental Measurements Laboratory, U.S. Department of Energy, New York, Environmental Quarterly Report EML 371, 1-51 (1980).

FURNIČA G.
"Principii metodologice in determinarea elementului radim".
Stud. Cerc. Chim. 17 (4), 307 (1969).

GESSEL T.F., PRICHARD H.M., HAYGOOD J.R.
Applications of commercial liquid scintillation counters to radon-222 and radium-226 analyses.
Proc. Health Phys. Soc. Symp. on Radiation Instrumentation, Ed. W. Wadman III, CONF-780110, 258-271 (1978).

GREGORY L.P.
"The determination of strontium,-90, radium-226, and lead-210 in human bone".
National Radiation Laboratory, New Zealand, Report No. NRL-RM/4 (1974).

HASL
"Procedures Manual" (Ed. by J.H. Harley)
U.S.Atomic Energy Commission, Health and Saf. Lab., HASL 300 (updated 1980).

HAVLIK B.
"Cumulation of radioactive substances by organisms of natural biocenosis of surface waters and its significance for determination of radioactive load."
J.Hyg. Epidemiol. Microbiol.Immunol. 11, 229 (1967).

HAVLIK B.
"Radioactive pollution of rivers in Czechoslovakia."
Health Phys. 19, 617 (1970).

HAVLIK B.
"Radium in aquatic food chains: radium uptake by fresh water algae".
J.Hyg.Epidemiol.Microbiol.Immunol. 17, 393 (1973).

HAYWOOD F.F., PERDUE P.T., SHINPAUGH W.H., ELLIS B.S., CHOU K.D.
"Radiological survey of the active uranium-mill tailings at Durango, Colorado".
Oak Ridge National Laboratory, USA, Report ORNL-5451 (1980).

HOMMA Y., MURAKAMI Y.
"Study on the applicability of the integral counting method for the determination of ^{226}Ra in various sample forms using a liquid scintillation counter".
J.Radioanal.Chem. 36, 173 (1977).

HOLTZMAN R.B., URNEZIS P.W., PADOVA A., BOBULA III C.M.
"Contamination of the human food chain by uranium mill tailings piles".
Argonne National Laboratory, Argonne, Illinois, USA:
Report NUREG/CR-0758, ANL/ES-69 (1979).

IVAN J., SLOVAK M., ABEL E., PATZELTOVA N.
"The intake of ^{226}Radium by ingestion and its evaluation in a selected group of population".
Čs. Hyg. 21, (8), 328 (1976).

IYENGAR M.A.R.
"Radium in natural and processing areas and its impact on human environment".
Report at the IAEA Forth Coordination Meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers", Vienna, Austria, (June 1980).

JARVIS A.N., SMIECINSKI R.F., EASTERLY D.G.
"The status and quality of radiation measurements of water".
Environmental Monitoring and Support Laboratory, Las Vegas,
Nevada, USA, Report EPA-600/4-76-017 (1976).

JOHNS F.B., HAHN P.B., THOME D.J., BRETHAUER E.W.
"Radiochemical analytical procedures for analysis of
environmental samples".
Environmental Monitoring and Support Laboratory, Las Vegas,
Nevada, USA, Report EMSL-LV-0539-17 (1979).

JONASSEN N., CLEMENTS W.E.
"Determination of radon-222 concentrations by an integrated
count method".
Health Phys. 27, 347-351 (1974).

JUSTYN J.
"Uptake of natural radioisotopes by aquatic organisms".
Radiobiol.Stud. 3, 145 (1973).

JUSTYN J., STANEK Z.
"Accumulation of natural radionuclides in the bottom sediments
and by aquatic organisms of streams".
Int.Rev.Ges.Hydrobiol. 59 (5), 563 (1974).

KAMETANI K.
"Analytical methods for determination of Ra-226 is soil".
Radioisotopes 24 (3), 59 (1975).

KAMETANI K.
"Determination of Ra-226 by means of measurement of Rn-222
radioactivity with a proportional counter".
Radioisotopes 24 (3), 59 (1975).

KELKAR D.N., JOSHI P.V.
"A rapid method for estimating radium and radon in water".
Health Phys. 17, 253 (1969).

KEY R.M.
"Estimating the standard deviation for ^{222}Rn scintillation
counting - a note concerning the paper by Sarmiento et al."
Earth Planet. Sci. Lett. 35, 184-187 (1977).

KEY R.M., BREWER R.L., STOCKWELL J.H., GUINASSO Jr. N.L.,
SCHINK D.R.
"Some improved techniques for measuring radon and radium in
marine sediments and in seawater".
Marine Chem. 7, 251 (1979).

KHADEMI B., MAHDAVI A.
"Increase of ^{226}Ra in the water intake by sheep".
Health Phys. 27, 522 (1974).

KIRCHMANN R., LAFONTAINE A., VAN DEN HOEK J., KOCH G.
"Comparaison du taux de transfert au lait de vache du ^{226}Ra de
l'eau d'abreuvage et du ^{226}Ra incorporé dans le foin".
Compt.Rend.Sciences Soc.Biol., 166 (11), 1557 (1972).

KIRCHMANN R., LAFONTAINE A., CANTILLON G., BOULENGER R.
"Etude du cycle biologique parcouru par la radioactivité".
Centre d'Etude de l'Energie Nucléaire, Mol, Belgique.
Rapport BLG 477, vol.II, Annexe Technique, (1973)

KIRCHMANN R., DARCHEVILLE, M., KOCH G.
"Accumulation of radium-226 from phosphate fertilizers in cultivated soils and transfer to crops".
"Natural Radiation Environment III", (Proc.Symp. Houston, Texas, USA, 1978), CONF-780422, 2, 1667 (publ.1980).

KOBAL I., KRISTAN J.
"Determination of ^{222}Rn concentration in hot spring waters using a scintillation chamber".
Radioanal.Lett. 10, 291 (1972).

KOBAL I., KRISTAN J.
"Extension of Raghavayya's method for the determination of radon in water".
Mikrochim.Acta (Wien) (1973), 219 (1973).

KOBAL I., SHAHIN M., KRISTAN J., SENEGAČNIK M.
"Sorption-emanation method for soluble radium in waters".
Health Phys. 27, 381 (1974).

KOIDE M., BRULAND K.W.
"The electrodeposition and determination of radium by isotopic dilution in sea water and sediments simultaneously with other natural radionuclides".
Anal.Chim.Acta 75, 1 (1975).

KOMURA K., SAKANOVE M., KONISHI K.
"Nondestructive ^{226}Ra/^{238}U dating of quartenary corals by gamma-spectormetry".
Proc.Japan Acad.Sci. 54 (9), 505 (1978).

KRISTAN J. KOBAL I.
"A modified scintillation cell for the determination of radon in uranium mine atmosphere".
Health Phys. 24, 103 (1973).

KU T.L., LI Y.H., MATHIEU G.G., WONG H.K.
Radium in the Indian-Antarctic Ocean south of Australia".
J.Geophys. Res. 75 (27), 5286 (1970).

KU T.L., LIN M.C.
"^{226}Ra distribution in the Antarctic Ocean".
Earth Planet.Sci.Lett. 32, 236 (1976).

KUROSAWA R.
"Error estimation of ionization method on the second inter-comparison of IAEA".
Report at the IAEA Third Coordination Meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers", Las Vegas, Nevada, USA, October 1978.

LENGER V., THOMAS J.
"^{226}Ra activity determination in nonequilibrium state by scintillation gamma spectroscopy".
Radioisotopy 11, (5), 797 (1970).

LEVINS D.M., RYAN R.K., STRONG K.P.
"Leaching of radium from uranium tailings".
Paper presented at the OCED-NEA Seminar on "Management, Stabilization and Environmental Impact of Uranium Mill Tailings",
Albuquerque, New Mexico, USA, July 1978.

LUCAS H.F.
"Improved low-level alpha scintillation counter for radon".
Rev.Sci.Instrum. 28, 680 (1957).

LUCAS H.F.
"What is the 'Lucas emanation method for ^{226}Ra "
Health Phys. 43, 278-279 (1982).

LUCAS H.F., WOODWARD D.A.
Effect of long decay chains on the counting statistics in the analysis of radium-224 and radon-222.
J. Appl. Phys. 35, 452-456 (1964).

LUCAS H.F., MARSCHAL J.H., BARRER L.A.
"The level of radium in human blood forty years after ingestion."
Radiatn. Res. 41 (3), 637 (1970).

LUCAS H.F., MARKUN F.
"^{228}Ra and ^{226}Ra in bone from radium cases".
Unpublished paper.

MARTIN S.S., HELM W.T., SIGLER W.F.
"Accumulation of ^{226}Ra in two aquatic systems".
Proc. Second Nat. Symp. on Radioecology, CONF-670503, 307 (Publ.1969).

MASTINU G.G.
"An emanation apparatus with simple operational procedure for measurements of low levels of ^{226}Ra".
Health Phys. 28, 97 (1975).

MASTINU G.G.
"Scintillation detector for radon-222 in air and water".
Natural Radiation Environment III (Proc.Symp., Houston, Texas, USA, 1978), CONF-780422, 1, 700 (publ.1980).

McDOWELL W.J.
"Alpha liquid scintillation counting: past, present and future", Liquid Scintillation Counting, Recent Applications and Developments. Vol. 1. Physical Aspects (Peng C.T., Horrocks D.L., Alpen E.L., Eds) Academic Press, New York (1980) 315-332.

MICHEL J., MOORE W.
"Sources and behaviour of natural radioactivity in Fall Line aquifers near Leesville, South Carolina".
Clemson University Water Resources Research Institute, Technical Report, No. 83, February 1980.

MICHEL J., MOORE W.S.
"^{228}Ra and ^{226}Ra content of ground water in Fall Line aquifers".
Health Phys. 38, 663 (1980).

MILLER M.L., FIX J.J., BRAMSON P.E.
"Lognormal analyses of naturally occurring radionuclides in soil and vegetaton of the Hanford Area".
Natural Radiation Environment III (Proc.Symp., Houston, Texas, USA, 1978), CONF-780422, 1, 826 (publ.1980).

MIYAKE Y., SUGIMURA Y., SARUHASHI K.
"The distribution of radon and radium in the ocean and its bearing on some oceanographic problems".
"Natural Radiation Environment III" (Proc.Symp., Houston, Texas, USA, 1978), CONF-780422, 1, 458 (publ.1980).

MOMENI M.H., ROSENBLATT L.S., JOW N.
"Retention and distribution of ^{226}Ra in beagles".
Health Phys. 30, 369 (1976).

MOORE W.S., REID D.F.
"Extraction of radium from natural waters using manganese impregnated acrylic fibres".
J.Geophys.Res. 78 (36), 8880 (1973).

MOORE W.S., COOK L.M.
"Radium removal from drinking water".
Nature 253 (5489), 262 (1975).

OHNO S., WATANABE H.
"Measurement of radium-226 in bone of Japanese people".
National Institute of Radiological Sciences, undated report.

OKUBO T., FURUYAMA K., SAKANOVE M.
"Distribution of ^{228}Ra in surface sea water of the East Indian Ocean".
Geochem.J. 13, 201 (1979).

OLTEANU M.
"A method for the determination of Ra^{226} in water".
Igiena XXIV (1), 15 (1975).

PAPASTEFANOU C., CHARALAMBOUS S.
"^{226}Ra leaching from fossil bones".
Nucl.Instrum.Methods 151, 599 (1978).

PARKS N.J., TSUBOI K.K.
"Emulsion scintillation counting of radium and radon",
Int.J.Appl.Radiatn.Isotopes 29, 77 (1978).

PARKS N.J., POOL R.R., WILLIAMS J.R.
"Variation of radon retention parameters for radium burdened dog skeletons as a function of exposure age and dosage level".
Radiatn.Res. 73, 274 (1978).

PASCHOA A.S.
"Preliminary results of concentration of radium-226 in waters of the Pocos de Caldas Region".
Report at the IAEA Second Meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Aquifers", Japan (1977).

PASCHOA A.S., BATISTA G.B., MONTENEGRO E.C., MIRANDA A.C., SIGAUD G.M.
"Ra-226 concentrations in the hydrographic basins near uranium mining and milling in Brazil".
Pontificia Universidade Catolica, Rio de Janeiro.
Nota Cientifica 02/79 (1979).

PAUL A.C., LONDHE V.S., PILLAI K.C.
"Radium-228 and radium-226 levels in a river environment and its modification by human activities".
Natural Radiation Environment III (Proc.Symposium
Houston, Texas, USA, 1978), CONF-780422, 2, 1633 (publ.1980).

PIETRZAK-FLIS Z.
"Radium-226 in Polish diet and foodstuffs".
Nuklonika XVII, (3-4), 227 (1972).

POPOVA O.N., KYRCHANOVA A.N.
"Analiz pasoki kak sredstvo izucheniya migratsii Ra^{226} v sisteme poshva-rastenie".
Ekologiya (6), 33 (1971).

POPOVA O.N., KYRCHANOVA A.N.
"Formy deponirovaniya Ra-226 v rasteniyah".
Agronomiya, 2, 110 (1974).

POWERS R.P., TURNAGE N.E., KANIPE L.G.
"Determination of radium-226 in environmental samples".
"Natural Radiation Environment III", (Proc.Symp. Houston, Texas, USA, 1978), CONF-780422, 1, 640 (publ.1980).

PRESTWICH W.V., KENNETH T.J.
"Radium determination in soil samples using a gamma-ray coincidence spectrometer".
J.Radioanal.Chem. 50 (1-2), 249 (1979).

PRICHARD H.M., GESELL T.F., MEYER C.R.
"Liquid scintillation analyses for Radium-226 and Radon-222 in potable waters".
Liquid Scintillation Counting, Recent Applications and Developments, Vol.1, Physical Aspects. Academic Press, New York, 347-355 (1980).

RAGHAVAYYA M.
Proc.Region.Seminar, Bombay, India, 1968, SM-114/17, p.227 (1968).

RAO S.R., BORKAR M.D., SHAH S.M.
"Distribution of ^{226}Ra in soil and water".
Proc.National Symposium on Radiation Physics, Trombay, India, 507 (1970).

REID D.F.
"Radium, thorium, and actinium extraction from seawater using an improved manganese-oxide-coated fibre".
Earth Planet.Sci.Lett. 43, 223 (1979).

ROESSLER C.E., SMITH Z.A., BOLCH W.E., PRINCE R.J.
"Uranium and radium-226 in Florida phosphate materials".
Health Phys. 37, 269 (1979).

RUSHING D.R., GARCIA W.J., CLARK D.A.
"The analysis of effluents and environmental samples from uranium mills and biological samples for radium, polonium and uranium".
Radiological Health and Safety in Mining and Milling of Nuclear Materials, (Proc.Symp. Vienna, Austria 1963), vol.2, p.187 (published 1964).

RYAN R.K., LEVINS D.M.
Extraction of radium from uranium tailings".
CIM Bulletin, 126-133 (1980).

SARMIENTO J.L., HAMMOND D.E., BROECKER W.S.
"The calculation of the statistical counting error for ^{222}Rn scintillation counting". Earth Planet. Sci. Lett. 32, 351-356 (1976).

SAUMANDE P., REIX F., BECK C.
"Etude de la radioactivité des eaux naturelles du Limousin; le Radium 226, l'uranium et le radon".
Bull. Soc. Pharmacie Strasbourg XVI, (2), 141 (1973).

SCHEIBEL H.G., PORSTENDORFER J., WICKE A.
"A device for the determination of low natural ^{222}Rn and ^{226}Ra concentrations".
Nucl.Instrum.Methods 165, 345 (1979).

SCHUTTELLKOPF H., KIEFER H.
"Die Dosisbelastung der Umgebungs bevölkerung durch naturlische und aus einer Uranunter suchungsrube emittiertes Ra-226."
Kernforschungzentrum Karlsruhe, Report KfK 2866 (1979).

ŠEBESTA F., BENEŠ P., SEDLAČEK J., HAVLIK B.
"Studies on the source, distribution, movement and deposition of radium in inland waterways and aquifers".
Report at the IAEA third Coordination meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers",
Las Vegas, Nevada, USA, (October 1978).

ŠEBESTA F., BENEŠ P., SEDLAČEK J., HAVLIK B.
"Studies on the source, distribution, movement and deposition of radium in inland waterways and aquifers".
Report at the IAEA fourth Coordination meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers",
Vienna, Austria, (June 1980).

SEDLAČEK J., ŠEBESTA F., BENEŠ P.
"Scintillation emanometric determination of radium-226 in waters using a new method of radium preconcentration".
J. Radioanal. Chem. 59 (1), 45 (1980).

SHAWVER J.M.
"The status and quality of radiation measurements in water - 1977",
Effluent and Environmental Radiation Surveillance, ASTM STP 698 (J.J. Kelly, Ed.) American Society for Testing and Materials, Philadelphia, 270-281 (1980).

SILL C.W. and WILLIAMS R.L.
"Rapid identification and determination of alpha emitters in environmental samples",
Rapid Methods for Measuring Radioactivity in the Environment (Proc. Int. Symp. Neuherberg bei München, 1971) International Atomic Energy Agency, Vienna 201-211 (1971).

SLADKOVA M., ABEL E., IVAN J., CHRAPAN J., ORAVEC J., HOLY K.
"Determination of low activities of radium-226 in water".
Cs.Hyg. 19, 480 (1974).

SMITH K.A., MERCER E.R.
"The determination of radium-226 and radium-228 in soils and plants,using radium-225 as a yield tracer".
J.Radioanal.Chem. 5, 303 (1970).

SMITHSON G.L.
"Radiochemical procedures for determination of selected members of the uranium and thorium series".
Canada Center for Mineral And Energy Technology,
CANMET Report, No.78-22, (1979).

SZABO E., TOKES B., PALL M.
"Continutul in ^{222}Rn, ^{226}Ra si activitatea beta-gama globala a apei instalatiilar centrale, a unor microcentrale, a unor microcentrale si a apelor de suprafata urai impartente din judetele Mures si Harghita".
Hidrotechnica (Bucaresti) 18, 191 (1973).

SZY D., URBAN A.
"Uber die Messung geringer Mengen Radium und Radon".
Mikrochim.Acta (Wien), 1971, 131 (1971).

TERNING J.A.
"Radiochemical analyses of radium, thorium, and protactinium in uranium milling process samples".
Int. J. Appl. Radiat. Isotopes 21, 507 (1970).

THOMAS J., MALATOVA I.,
"Evaluation method of the gamma spectrometrical determination of radium in state of non-equilibrium".
Radioisotopy 11, (5), 815 (1970).

THOMAS J., ROTH Z., MALATOVA I., LENGER V.
"Analysis of gamma spectra of ^{226}Ra or ^{224}Ra in non-equilibrium with their decay products".
Health Physics Problems of Internal Contamination, (undated separatum).

TREUELLE M.A.
"Content of ^{226}Ra in selected food produced in the South-Bohemian Region".
Čs.Hyg. 22, 141 (1977).

VANDERBORGHT O., COLARD J., BOULENGER R.
"Human faecal ^{226}Ra excretion shortly after a $RaSO_4$ dust contamination, with alginate treatment".
Health Phys. 23, 240 (1972).

VDOVENKO V.M. and DUBASOV Y.V.
"Analytical chemistry of radium"
(Transl. Ed. Malament D.) Wiley, New York (1975).

VERNET J.P., DAVAND E., COSANDEY M., BERLIE J.
"Analyse de la radioactivité gamma des sédiments des lacs Leman et de Moret".
Eclogae Geol. Helv. 68/1, 87 (1975).

VILENSKII V.D.
"Raspredelenie svinca-210 i radya-226 v nekaterih pochvah".
Geokhimiya, (12), 1507 (1969).

VILENSKII V.D., ANIKIEV V.V.
"Svinets-210 i radii-226 v vodnih otlozheniya presnyh vodoemov".
Geokhim. 8, 1259 (1974).

VLČEK B.
"Radiochemical analyses by means of adsorption plates, I. Method and determination of radium".
Collect. Czech. Chem. Commun. 28, 3326 (1962).

WEAST R.C.
"CRC Handbook of Chemistry and Physics".
CRC Press, Cleveland, 58th Ed. (1978) B.

WIEGEL F.
"Radium".
Gmelin Handbuch der Anorganischen Chemie: 31.
Springer-Verlag, Berlin (1977a).

WEIGEL F.
"Radium".
Chimiker Z., Sonderdrick 101, 486 (1977b).

WILLIAMS A.R.
"An international comparison of ^{226}Ra analyses by the emanation method".
Health Physics, 41, 178-183 (1981).

WILLIAMS A.R., O'BRIEN B.G., MEARS K.F.
"Random errors in radiochemistry: the Lucas emanation method for ^{226}Ra ".
Health Physics, 41, 47-57 (1981).

WILLIAMS A.R., O'BRIEN B.G.
"Reply to H.F. Lucas"
Health Phys. 43, 279-280 (1982).

WLODEK S., GRYZBOWSKA D., BYSIEK M.
"Influence of human activity upon ^{226}Ra migration in the environment".
Nukleonika, XV (9-10), 675 (1970).

YAMAMOTO T., YUNOKI E., ISHIDA T.
"Determination of uranium and radium in soil."
(in Japanese with a summary in English).
Annual Report of Okayama Prefectural Research Center of Environment and Public Health, No. 1, 159 (1977).

YASSTREBOV M.T.
"Natural radioactivity of some soils and landscapes of Tambov Forest-Steppe".
Vestn. Mosk. Univ. Biol. Pachv. (6), 91 (1973).

ZETTWOOG, P.
"Intercomparison of analytical methods for radium within the IAEA Coordinated Research Program on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers".
Report at the IAEA Third Coordination Meeting on "The Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers", Las Vegas, New Mexico, USA (1978).

ZIMMERMAN J.B., ARMSTRONG V.C.
Canada Center for Mineral and Energy Technology,
CANMET Report 76-11 (1975).

Chapter 3

DISTRIBUTION IN NATURE

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3.1. INTRODUCTION

With nuclear energy acquiring a significant role in the energy map of the world, there is a growing emphasis on increased Uranium production. As a consequence, more and more process wastes from the Uranium industry are building up in tailings dams or impoundment basins in various parts of the world. Although each of the radionuclides present in the tailings, i.e. Natural U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po is of equal concern, ^{226}Ra forms the critical nuclide in setting permissible standards for members of the public (ICRP 1959). This is based on the fact that ^{226}Ra has a high degree of radiotoxicity, is bone-seeking, has a long half life of 1620 years and as an alpha emitter has a high potential for biological damage. As a homologue of Ca, an essential metabolic element, Ra closely follow Ca metabolism in man with eventual deposition in bone followed by decay to ^{222}Rn and a series of shortlived Rn daughters, causing significant radiation exposure.

In the context of environmental disposal of the active wastes from uranium processing facilities, the surface waterways constitute a vital link in the migration and build-up of Ra in various environmental components, such as sediments, biota, dietary materials, etc., of relevance to human exposure. To some extent the ground waters also play an important role in receiving the effluent seepage from tailings ponds, causing Ra to move in the ground water system. Besides the Ra originating from the first stage of the nuclear fuel cycle, areas of higher background radioactivity due to occurrence of uranium and thorium containing minerals, are also sources of elevated Ra levels in the neighbouring environment. Therefore a study of the distribution of ^{226}Ra in the natural aquatic environment, in particular its biogeochemical cycle, is of considerable importance in the evaluation and control of population exposures.

Under this coordinated programme, the main emphasis has been confined to groundwaters, surface streams and stream biota. The data included in this review, is also generally confined to those of the participating countries, namely, Australia, India, Japan, Czechoslovakia, France, Yugoslavia, Brazil, South Africa, USA and Belgium, as a complete overview of the worldwide data has not been planned at this stage. However it is hoped that such review will be possible in future, under the Agency's programme.

However in the context of natural distribution data of ^{226}Ra in these environments, the information available is not fully satisfactory for most components. Wherever such information exists, as in the case of ground and surface water, the data is presented with supporting information. But in the case of sediments and biota much of the data comes from contaminated situations with a few observations made as part of a baseline survey.

3.2. GROUND WATERS

3.2.1. ^{226}Ra Distribution in Selected Geographic Regions

In the aquatic domain, the ground waters play an important role from the viewpoint of their exploitation by man for a variety of purposes. In many areas of the world the ground waters find extensive application in agriculture, and in areas of scarce surface water resources the ground waters form the main source of drinking water for the community, besides meeting it's industrial and recreational requirements. In view of these, and in addition due to the highly toxic nature of ^{226}Ra in public water supplies, the study of ^{226}Ra in ground waters has assumed considerable significance; for e.g. the USEPA (1976) has laid down that in community water supplies ^{226}Ra and ^{228}Ra together must not exceed 0.185 Bq/l(5.0 pCi/l). As a guideline it is also recommended that if water contains greater than 0.185 Bq/l alpha activity, ^{226}Ra must be determined and if ^{226}Ra is greater than 0.111 Bq/l (3 pCi/l), ^{228}Ra must be determined. However in cases of suggested presence of ^{228}Ra, States are recommended to determine ^{228}Ra and/or ^{226}Ra if gross-alpha is greater than 0.074 Bq/l (2 pCi/l).

Radium in groundwaters can arise from natural sources, resulting from interaction of groundwaters with Ra bearing materials like rocks, soils, orebodies etc. It can also arise indirectly from man's exploitation of radioactive minerals of uranium, thorium etc. for nuclear power generation. Besides there is considerable radioactivity in other conventional minerals of commercial importance such as phosphatic minerals, apatite ($Ca_5(PO_4)_3F$, Cl,OH), copper, gold, lignite, coal, bauxite and such other ores due to the presence of uranium and its longlived daughter products, like ^{226}Ra, ^{230}Th, ^{210}Pb, ^{210}Po etc. Mining and processing of these minerals for metal recovering can also bring about enhancement of the Ra levels in the environment well above the normal background levels. In the case of natural unmined ore deposits Ra can enter the ground waters by way of leaching of the Ra bearing rock strata by the ground water aquifer. Geothermal springs are considered to be another source of natural radioactivity, including among others, ^{226}Ra and ^{222}Rn. Considerable attention is being devoted by recent investigations towards studying the radiological exposure significance of thermal springs and spas, which serve as tourist attractions in many countries.

In common with any other mineral processing industry, the mining and milling of large quantities of uranium ores, increasingly in practice in many areas of the world to meet growing energy needs, leaves behind a large volume of wastes. Although these wastes are not characterised by high specific activity, the main concern arises from the near quantitative presence of ^{226}Ra in the waste effluents and its possible impact on environmental health. If the waste treatment and control practices are not efficient, most of the dissolved ^{226}Ra will

eventually find its way through mill tailing flow, reaching the nearby streams (Tsivoglou E.C., et al., 1964). Even where large tailings impoundment ponds are maintained as part of environmental control measures Ra can reach groundwaters by direct seepage of the pond effluents. Besides leaching of residual tailings by rain water and percolation of these waters into the ground water system, can also raise the background Ra levels in ground waters.
In view of these the study of Ra in the aquatic environment would be incomplete without a detailed reference to its occurrence and movement in ground waters. The main areas of study in different parts of the world under the Coordinated Programme and their study context are given in Table 3.1.

The large body of data generated by these studies have geen processed using the statistical data concentration programme (ZCH 2 and ZCH 3/2) developed at the Zentralabteilung für Chemische Analysen, KFA Jülich, West Germany (Sansoni B., et al, 1981). Examples of the processed data are presented as (1) areawise histogram (Fig. 3.1), (2) lognormal probability plots (Fig. 3.2), (3) relative frequency plots of each study (Fig. 3.3). The range of concentrations and their central values with dispersion and the type of frequency distribution are given for the composite data in Table 3.2.

3.2.2. Discussion

The ^{226}Ra levels in the Florida Study are in the range of less than lower limit of detection to 2.8 Bq/l. Extensive application of statistical methods on the Florida ^{226}Ra data analysis (Kaufmann R.F. and Bliss J.D., 1977), has shown no impact on the Upper and Lower Floridan aquifers, either as a result of phosphate mining and waste management practices, or due to unmined mineralised areas. However where occasional high ^{226}Ra concentrations are noticed as in Lower Floridan aquifer, they are stated to be associated with natural factors unrelated to phosphate mineralisation or the Central Florida phosphate industry. Tanner (1964) has pointed to elevated levels of ^{226}Ra in ground waters with chloride enrichment. The Florida study also demonstrates that in general ^{226}Ra levels increase with salinity, which in turn varies with well depth and position in the well regime within the Floridan aquifer system.

^{226}Ra concentrations in ground waters of Sarasota county were found to be two orders of magnitude greater than in the primary study area for the water table and almost an order of magnitude greater for the Floridan aquifer. Ra in the water table aquifer is significantly greater in the coastal area compared to inland area. Occurrence of monazite sands in the beaches near Venice in Sarasota county has been indicated as a potential ^{228}Ra source. The study speculates on the possible effect of increased concentration of dissolved solids, calcium in particular on enhanced Ra levels. Good correlation of ^{226}Ra concentration with total dissolved solids is indicated (γ =0.82), tending to support a cause-effect relationship.

Investigation of radioactivity associated with geothermal waters in Western United States (O'Connel and Kaufmann 1976), covers the hot springs and wells located in Arizona, California, Colorado, Idaho, Nevada, New Mexico, Oregon and Utah. The ^{226}Ra distribution data for example, from hot springs in northern California approximates to a straight line fit on a lognormal frequency distribution plot (Fig. 3.4). The linearity implies that the data are from a single population (Denham and Waite, 1975). However there appears a slope change around 0.1 pCi/l (0.1137 Bq/l), which could indicate an outside influence or variation in the existing source. In the case of ground waters, according to authors, such a change may be attributed to variations in the flow system, regional rock type or nearby magmatic activity. ^{226}Ra concentrations for geothermal waters as a whole are in the range of 0.0015 to 55.5 Bq/l. No definite conclusion regarding radioactivity associations in the geothermal waters could be obtained according to the study report.

The Australian data from Yeelirrie (Brownscombe, A.J. et al., 1978) show a wide range of ^{226}Ra concentrations (0.019 -33.4 Bq/l). ^{226}Ra levels tended to be generally high in the region of ore body. While making a concluding reference to Table 3.2, it is observed that the concentration data for ^{226}Ra in groundwaters for the study areas lies in a large range, of 0.0005 to 55.5 Bq/l. The data approximates to a lognormal distribution within a statistical probability of 95% (α =0.05) for most areas with a single exception, i.e. geothermal waters. The Kolmogorov-Smirnov goodness-of-fit test also supports this observation. Hence the arithmetic mean $\bar{x}$, cannot be used reliably for characterising the central value of the data distribution. Taking the median $\tilde{x}$ as the central value of choice, some conclusions can be drawn. They are:
(a) The ^{226}Ra concentrations in groundwaters are increasing in the order of:

Brazil $<$ Grants $<$ Geothermal
Texas $<$ Florida $<$ Yeelirrie $<$ Florida-Sarasota.

(b) Within a narrow range of concentrations, from 0.0059 to 0.0139 Bq/l, are Brazil, Grants and Geothermal; these are followed by Texas and Florida with 0.0444 and 0.0518 Bq/l respectively. The two areas with the highest ^{226}Ra concentrations are Yeelirrie and Florida (Sarasota), at 0.303 and 0.381 Bq/l respectively.

3.3. SURFACE WATERS

3.3.1. Baseline ^{226}Ra Levels in Surface Waters in Some Mining Areas

Surface Waters, unlike ground waters are the immediate recipients of land run offs, industrial and municipal effluents, residuals from agricultural applications of fertilizers, pesticides etc. At the same time they are also sources of nearly unlimited potential for human usage such as in community water supplies, agriculture, industry, transportation, recreation etc.. However with the rising population and growing industrialisation many waterways are being increasingly polluted carrying a variety of pollutant loads and toxic materials.

The surface streams play a vital role in the biogeochemical cycling of many essential and toxic elements in the environment. In view of these and with the aim of carrying out radiation exposure assessments of the population, surface streams monitoring has received considerable attention in uranium mill environment studies, particularly with reference to Ra. However there is still paucity of background Ra data for non-polluted surface waters. Wherever such data exist they are few, from site specific studies and usually are available, while describing a pre-operational situation of a projected uranium mining operation. Some of these data coming from Brazil, Australia and Yugoslavia are given in Table 3.3. Examples of frequency distribution for two of the three data sets are given in Fig. 3.5 and 3.6.

3.3.2. Discussion

^{226}Ra concentrations of Brazilian river waters in the vicinity of uranium mining area at Pocos de Caldas have been measured as a baseline study in 1977-78 (Paschoa A.S. et al., 1979). The concentrations are within a range of 0.0074 to 0.222 Bq/l. But in most of the river water samples, ^{226}Ra levels were generally under 0.037 Bq/l with the exception of small streams, originating in the region of exploratory uranium mining where the ^{226}Ra concentration was 1.1 Bq/l. Limited seasonal studies did not appear to show much variation in Ra concentrations in these waters.

The Yugoslavian data, also part of a baseline study conducted in 1977, come from the surface waters of Sava River and other minor rivers in the region of Slovenia, the site of an explorative uranium mine at Žirovski Vrh (Kobal I., et al., 1978). The ^{226}Ra levels are in the range of 0.00037 to 0.115 Bq/l in the surface waters of the area. These values are comparatively lower than ^{226}Ra concentrations generally observed in surface waters in the region of uranium deposits elsewhere. Negligible contamination of Sava river is concluded from the study. The Australian studies relating to the Alligator Rivers area of the Northern Territory Uranium Province (Davy D.R. and Conway N.F., 1974) show ^{226}Ra concentrations in surface waters in the range of 0.0033 to 0.3 Bqhl. The central values are also very much above the Brazilian and Yugoslavian data. Ra levels tend to rise during the dry season but more studies are needed to draw meaningful conclusions on seasonal variations.

Although the areas of study as well as the number of samples are far too few for surface waters compared with ground waters, a statistical analysis has been attempted. A reference to Table 3.3 with median value $\tilde{x}$ as the choice parameter, shows that Yugoslavia has the least concentration, followed by Brazil and Australia. The Brazil value perhaps ought to be much closer to Yugoslavian figure than it appears, but the situation lacks clarity, because of the higher detection limit of 0.0074 Bq/l in the Brazilian data; again the Australian data have some of the highest concentrations.
Some of the background measurements in the Jaduguda and Alwaye surface waters in India, show dissolved ^{226}Ra concentrations in the range of 0.005 to 0.07 Bq/l respectively (Iyengar M.A.R. and Markose P.M. 1970, Paul A.C. et al 1978).

In the context of investigations on natural distribution of Ra in surface waters in general and not bound with any site specific industrial or technological activity, the case study of Miyake et al (1964) in Japanese rivers is of considerable value. The study involved ten rivers spread over four Japanese islands, namely Hokkaido, Honshu, Shikoku and

Kyushu, and was aimed at measuring U, Ra and Th distribution in river waters with a view to understand their geochemical cycles. The study yielded Ra concentrations in the range of 0.0014 to 0.0051 Bq/l. The weighted mean of 0.003 Bq/l for Ra in Japanese rivers, according to the authors, does not appear greatly different from the mean value of 0.0026 Bq/l reported for continental rivers. The result showed further that radium content of the river waters is equivalent to only 34 percent of the uranium supported radium in the equilibrium state. However slightly enhanced dissolved Ra concentrations were observed in river waters from granitic region, as compared with those from regions covered by volcanic eruptives.

In conclusion, surface waters display a more regulated and a narrow range of ^{226}Ra concentrations unlike ground waters, where the concentration spread is fairly large. In addition ground waters in many regions are rich in Radon concentrations posing problems of human exposure. High concentrations of ^{230}Th, ^{210}Pb, and ^{210}Po, other important members of uranium decay series, are also not uncommon in certain ground water supplies.

3.4. STREAM SEDIMENTS

3.4.1. ^{226}Ra Distribution and Movement Behaviour in Stream Sediments

In a natural stream environment, many dissolved elements, including some of the toxic trace metals, tend to associate themselves with the particulate phase, by a process of sorption on the settled or suspended particulate materials normally present in the stream. The mechanism by which this is brought about can be broadly termed as processes of adsorption, exchange, and coprecipitation. The rapidity and efficiency with which this takes place depends, apart from the physico-chemical behaviour of the element in question, largely on the characterisation on the particulates existing in natural stream conditions. In general the stream particulates can be categorised as detrital, authigenous, and biogenous following their origin; and under naturally obtaining stream conditions, each of the above type of sediment material normally present in various proportions, displays a certain sorption capacity for a given element. A sum total of their capacity for the uptake of a specific element is normally reported as the Kd factor for a stream environment under study, which is the ratio of concentration of the element in the particulate material and in the water medium.

However in most water bodies there is a certain degree of equilibrium between the dissolved and particulate elemental forms. Therefore a study of the particulate associated element is of considerable importance in understanding the nature, behaviour and movement of the element of interest. In case of radium, it has been the general experience that the stream sediments account for a substantially large fraction of Ra in the stream environment, in the vicinity of uranium mining and milling operations. Here the ore tails following uranium recovery, are led into large impoundment basins and in course of time, there is a gradual seepage of ^{226}Ra and other radiotoxins into the nearby flowing streams both in the dissolved and suspended forms. The finely suspended material, which is relatively rich in Ra, compared to the coarse fraction, eventually settles down in the lower reaches of the river in course of time. The Ra present initially in the dissolved state also tends to adsorb on to the suspended or settled particulates, and under most natural stream conditions this takes place quite effectively, thus making the stream sediment as the major reservoir of Ra reaching the aquatic environment.

In the ecological context and with reference to the population exposure, the sediment phase offers an effective medium for the transfer of radium up the food chain. The bottom sediment environment provides the ideal habitat and food requirements for aquatic biota, such as clams, prawns, crabs, and certain types of fishes. The degree and state of enrichment of Ra in the sediment may be expected to reflect in the tissue concentrations of Ra in these organisms. Some of the results of stream sediment studies from Australia, Belgium and India are summarised in Fig. 3.7. (Dafy D.R. and Conway N.F. 1974, Kirchman R. et al 1979, Markose P.M. et al 1978, Paul A.C. et al 1978). The Kd factors, from the Australian and Indian data are given in Table 3.4.

3.4.2. Discussion

The range of ^{226}Ra concentrations in different geographic locations appear to be more or less in a uniform range, with exceptional values where contamination sources are present. Briefly the ^{226}Ra contents of the stream sediments given in Fig. 3.7. are:

Jaduguda, India:	0.015 - 2.0 Bq/g
Periyar River, Alwaye, India:	0.001 - 1.5 Bq/g
Alligator Rivers, Australia:	0.001 - 0.093 Bq/g
Monsin, Belgium:	0.033 - 0.452 Bq/g

The data however consists of both background and operational data, particularly from India. Hence the maximum values here should be regarded as technologically enhanced concentrations due to mining and milling activities. The Kd factors are in the range of (0.03 - 1.57) x 10^3 for Australia and (5.4 - 7.1) x 10^3 for Jadaguda. However the Australian data belongs to two different types of water environments, but the data do not indicate any significant departure between them. Tsivoglou et al (1964) after analysis of ^{226}Ra in hundreds of stream sediments of Western United States, found the natural distribution of ^{226}Ra in these sediments as 0.059 Bq/g. In view of the consistent data, the study concluded that stream sediments could play a very sensitive role as pollution indicators of river streams, in uranium mill neighbourhoods. Kirchmann (Pers. Comm.) has reported that in the Albert Canal of Belgium, upstream ^{226}Ra concentrations in bottom sediments ranged from 0.015 Bq/g at 0-10 cm depth to 0.011 Bq/g at 40-50 cm depth.

3.5. BIOTA

3.5.1. Fishes

In view of the widely differing Ra activities in waters in a range of aquatic environments, highly fluctuating Ra concentrations can be expected in the resident biota of such waterbodies. Among the various samples of biota normally examined, fishes have an important place of investigation for two reasons. Firstly, fishes occupy a higher trophic level in an aquatic ecosystem and therefore their tissue Ra concentrations may be expected to reflect a cumulative series of events in the movement of Ra through the aquatic food chain leading to either its gradual accumulation or discrimination, at the higher trophic level. Secondly fish constitutes one of the very important components of human diet and therefore a study of Ra distribution in fish tissues is of vital significance in evaluating the radiological exposure of the population.

^{226}Ra contents of a variety of fish species mostly from fresh-waters, from the study regions under this programme, are presented in Table 3.5. For comparison however ^{226}Ra levels in a nearshore marine environment are also included.

In these studies there appears a wide range of ^{226}Ra concentrations. For muscle, it ranges from 0.019 to 5.9 Bq/kg (wet), and for bone from 0.55 to 51.8 Bq/Kg (wet). Tissuewise however bone displays higher concentration levels which is understandable considering the analogous behaviour of Ra with Ca. However, whether the differences in the activity levels among the samples from the same study region could be attributed to temporal, seasonal or species factors, needs elucidation.

As part of this study, an investigation conducted at Jaduguda, India, shold be of interest in understanding the concentration of ^{226}Ra in a single fish species, in a steady stream environment over an extended period of time, i.e. about a month. Having observed that a particular type of fishes of Ophiocephalus sp. were inhabiting the mine water stream, wire mesh screens were placed 200 metres apart at the stream location, to restrict the movement of fish within this area, but without interfering with the natural flow characteristics of the stream. Periodically samples of the fish species were drawn from the area and analysed for their muscle and bone ^{226}Ra concentrations. Analyses of six catches of the fish species carried out during the month-long study are given in Table 3.6.

The results demonstrate an interesting range of ^{226}Ra concentrations obtained under natural field conditions; Muscle from 2.6 to 7.9 Bq/kg (wet); bone from 20.6 to 39.8 Bq/kg (wet). However the most striking aspect of the data is the ratio of Ra content in bone and muscle, which remained remarkably constant in a narrow range of 5 to 6.1, barring a single case, where it was 7.9. The concentration factors also appear to be in a reasonably close range, for muscle they vary from 5 to 15 and for bone from 40 to 77.

Similarly, a study has been carried out in Australia to observe the pattern of ^{226}Ra accumulation in fishes under premining and postmining conditions. The results are given in Table 3.7. The data reported however do not bring out any marked contrast between the two situations. Speaking of intraspecie differences for Barramundi, there is a wide range of concentrations tissuewise, in both the operational situations. As a whole there appears in general, relatively little enhancement of ^{226}Ra in the fishes in the postmining phase. This is to be attributed to the practically very little change in dissolved ^{226}Ra concentrations in the stream waters. The range of concentration factors are quite wide; premining: 11 to 350; postmining: 36 to 646. There appears a slightly higher concentration level of ^{226}Ra for the Black Bream, but the data is meagre for a definite inference.

Because Ra and Ca are chemically similar, a study of the Ra/Ca ratios in the environment and in fishes would be of considerable interest. De Bortoli et al (1972) have studied ^{226}Ra distribution with respect to Ca in fishes of some of the lakes in Italy. The data are reported in Table 3.8. Considering the movement of Ra in the biological chain, the ratio of Ra concentration relative to Ca should be independent of some variables which affect the absolute concentration ratio, thus reflecting the very biological discrimination of Ra against Ca. In this context, the observed ratio, O.R., has been found to be useful. By definition:

O.R. = (Bq/g Ca in sample)/(Bq/g Ca in precursor).

In the above study, the O.R. between fish-water is 0.20, which is derived as an average of four lakes and whose range is pretty large, 0.09 to 0.31. It seems therefore that the fish-water concentration factor is related to the Ca concentrations in the different lakes. This correlation is shown in Fig. 3.8, from which it is observed that lake Monate deviates markedly from the other three lakes. A correlation coefficient of 0.998, makes the study significant at an $\alpha = 0.05$ probability level. For comparison purposes, ^{90}Sr data taken from another study (Gaglione P., et al., 1969) are also shown in the same figure.

As the available fish data come largely from a mixture of polluted and non-polluted environments no precise conclusions could be drawn about the natural level of ^{226}Ra distribution in fishes.

3.5.2. Algae and Plankton

3.5.2.1. Algae

Of the various biological media useful in environmental monitoring, algae offers itself as possibly one of the most sensitive bio-indicators in studying stream pollution situations. With the exception of stream locations where the physical and chemical conditions of the stream do not support the growth of algal mass, in most situations it is relatively easy to locate and sample algal material for studying the pollution status of the stream. Among the various stream biota, algae has a unique quality in that it concentrates from the medium, primarily the dissolved form of the element under study. In many pollution monitoring requirements, with a view to control public health hazards, the permissible standards are based on the actual dissolved concentrations of the toxic element. The property of algae in concentrating mainly the dissolved fraction of the pollutant nuclide would be of considerable significance and advantage in pollution assessment and control measures in uranium mining and milling activites.

Among the early studies, Tsivoglou et al (1964) used filamentous algae in monitoring the Animas River radioactivity in the vicinity of uranium mills at Colorado, U.S.A. ^{226}Ra concentrations of the order of 0.148 Bq/g of algal ash were recorded for uncontaminated streams whilst concentrations as high as 129.5 Bq/g of algal ash were observed for the polluted locations of Animas river, which showed concentration potential of algae of a high order for ^{226}Ra. Following this, uranium mill environment studies in general have utilised algae radioactivity to serve as a useful indicator of the environmental impact from uranium mill effluent discharges.

Results of one such study from Jaduguda, India, is given in Table 3.9 (Markose P.M. et al 1978). From the data one could observe widely differing ^{226}Ra concentrations in the algae as well as in the stream water, depending upon the proximity of the location with respect to the tailings pond effluents or minewater stream which are the sources ^{226}Ra in the stream environment. It could generally be seen that there is a gradual fall in ^{226}Ra concentrations in algae as one proceeds downstream with a corresponding fall in ^{226}Ra concentrations in the water medium. The concentration factors (CF's) calculated for each sample location are also given in the table. These CF's are found to be in a reasonably good range of 800 to 3100, which are in general agreement with those of Tsivoglou, et al., (1964) i.e. 500 - 1000. These relatively high concentration factors (about 10^3) serve to demonstrate the role of algae, Spirogyra sp. in particular, as a good indicator of Ra contamination of the aquatic environment.

3.5.2.2. Plankton

Since plankton constitutes an important component of mussel's diet, ^{226}Ra concentrations of plankton would be of significance. ^{226}Ra levels in the nearshore marine plankton have been studied at Kalpakkam, India, and the results are as follows:

Sample type	^{226}Ra in		Concentration Factor (CF)
	Plankton Bq/Kg (wet)	Water Bq/l	
Phytoplankton (composite)	1.32	0.0016	825
Zooplankton (composite)	1.55	0.0016	968

Kirchmann, et al., (1973, 1971) have reported a concentration figure of 2.78 Bq/g (wet) for ^{226}Ra in plankton in the Tessenderlo region of Belgium. However the ^{226}Ra concentrations in these fresh waters are reported in the range of 0.040 Bq/l - 1.0 Bq/l. Accordingly the CF works out to 2775 - 6820 which is much higher than observed in the marine location at Kalpakkam.

Since phytoplankton are primary producers and have a high concentration potential for many toxic trace elements, more data are essential in elucidating their role in the migration of Ra in the aquatic environment.

3.5.3. Aquatic Macrophytes

Aquatic macrophytes are aquatic plants characterized by a high order of metabolic activity. It was seen earlier in the Indian study that certain types of algae display a high degree of uptake of ^{226}Ra from ambient waters with concentration factors of about 10^3. It would be therefore interesting to examine the ^{226}Ra activity concentrations in the aquatic macrophytes and assess their potential for a possible role in environmental investigations on the migration of Ra. However, with the exception of some data from Belgium and France, information on this class of biota is sparse. Kirchmann et al (1973) have reported ^{226}Ra levels in some of the aquatic macrophytes from Tessenderlo region of Belgium:

Sparganium: 6.66 and 40.7 Bq/g (dry)
Callitriche: 14.8 Bq/g (dry)
Ranunculus aquatilis: 7.4 Bq/g (dry)

^{226}Ra concentrations in the Tessenderlo waters are reportedly between 0.41 and 1.0 Bq/l. In the absence of the water content data and the corresponding fresh weights for these samples the actual concentration factors, cannot be derived. However in a similar study on *Callitriche* species carried out in France (Progress Report to IAEA, 1977) ^{226}Ra was found to be 49.95 Bq/g (dry) or 1.41 Bq/g (wet) and with a ^{226}Ra concentration of 14.06 Bq/l in water, the concentration factor was calculated to be 100. Applying this dry to wet ratio on the Belgian data, one can obtain the concnetration factors for the above three species as follows, assuming an average water concentration of ^{226}Ra as 0.7 Bq/l:

Sparganium	(a) 266	(b) 1628
Callitriche	592	
Ranunculus aquatilis	296	

A comparison of these concentration levels and concentration factors (CF's) with the earlier algal data tends to show generally a lower Ra uptake capacity of the aquatic macrophytes. However with CF's in the range of 266-1628, these macrophytes could be still useful in environmental surveillance in addition to or in the absence of other samples of biota.

3.5.4. Molluscs

3.5.4.1. ^{226}Ra distribution characteristics in marine and fresh water molluscs

Among the aquatic fauna, relatively higher radioactivity concentrations are observed in general in shell fishes, when compared with fishes. This phenomenon of higher activity incorporation may be due either to their special food habits or some characteristic concentrating metabolic properties or by an active combination of both processes. Hence the shell fish has found increasing utility in environmental radioactivity measurements. For instance in the UK studies at Bradwell Nuclear Power Station, oysters were found to be extremely useful indicators of ^{65}Zn in the aquatic environment, with a concentration level of 0.166 Bq/g (wet), (Mitchell, 1969). Oyster sampling is now routinely used for monitoring many reactor environments for radioactivity due to ^{65}Zn, ^{32}P, ^{110m}Ag, ^{55}Fe, etc.

3.5.4.2. Discussion

However, there is possibly little information on the natural radioactivity in shell fishes particularly in a freshwater environment. In this context the Australian data of Conway, Davy et al (1974) is of considerable interest. The results are part of a study in the Alligator

Rivers area of the uranium province in northern territory. A representative cross section of these data is given in Table 3.10. A very wide range of ^{226}Ra concentrations from (1.1 to 165.8 Bq/kg, wet) and concentration factors of 10 to 12100 are observed. However the high degree of scatter in the data points to factors other than merely environmental concentration of Ra. The analyses did not also demonstrate any conclusive evidence of discrimination of Ra in the organism during the matabolism of Mg and Ca.

The nearshore marine environment is a familiar habitat for many aquatic organisms including mussels, clams, snails, etc. commonly grouped under mulluscs. The natural distribution of ^{226}Ra in these organisms would be interesting to study. Some of the data from the Kalpakkam environment in India are given in Table 3.11.

It is observed from the presented data that, in comparison with freshwater data from Australia, the ^{226}Ra levels in these organisms are in a narrow range; soft tissues range from detection limit to 0.10 Bq/kg (wet); shell, from 0.25 to 1.12 Bq/kg. The concentration factors are also in a close range, particularly in the case of soft tissues, from 46 to 63. This may possibly be attributed to the highly steady ^{226}Ra levels normally existing in the waters of a marine environment. The shell expectedly accumulated more Ra due to its higher Ca uptake. Ratios of Ra in shell and soft tissue vary from 2.5 to 10.

3.6. CONCLUSIONS

Whilst the ^{226}Ra levels are low for surface waters and lie in a relatively narrow range of concentrations, the ground waters display a wide range, even of a higher activity order depending upon the source characteristics in the region of study. ^{226}Ra distributions in the stream matrices - sediment and biota, were found to be of considerable interest as a majority of the samples showed high concentration factors in a range of environments. The stream sediment was found to be particularly useful in detecting stream pollution from uranium mill effluents. Among the biota, the algae Spirogyra Sp exhibits a remarkable concentration potential for ^{226}Ra (CF: 800-3100) and thus could serve as a highly useful indicator species for environmental radium. Other samples of biota like mussels, fish, aquatic macrophytes also appear to possess good monitoring qualities.

However the information presented here is a small cross section of the available data and is neither complete nor adequate form environmental modelling and dosimetric considerations. Such an attempt requires a reasonably large body of data collected by a number of laboratories using mutually comparable methods of sampling, analysis and data evaluation. In this context the following suggestions may be worthy of consideration:

1) The natural distribution data for ^{226}Ra are comparatively few and needs reinforcement for a variety of environmental media from different environments, to make baseline exposure evaluations realistic.

2) The data coming from operational investigations have served well in highlighting the contamination aspects of many an ecosystem, demonstrating the interesting Ra uptake behaviour of some species of biota. Besides studying these species more intensely, attention should be directed to other additional varieties of flora and fauna, specific to each aquatic environment, to obtain an intimate understanding of environmental concentration pathways. The contaminated stream situations near uranium mills and tailings dams, and the contiguous background regions, should provide excellent opportunities for these studies supported by control experiments in the laboratory, towards a better understanding and evaluation of the ecological parameters.

3) In addition to ^{226}Ra, other nuclides of importance such as ^{228}Ra- particularly in high natural background areas - ^{230}Th, ^{210}Pb, ^{210}Po, ^{222}Rn, U (nat), Th (nat), etc., should be also investigated on similar lines to get a comprehensive coverage of the environmental natural activity as a whole for a proper avaluation of environmental radiation exposures.

Table 3.1. ^{226}Ra in Groundwaters-Study Areas

	Area of study	Purpose of study
1.	Grants Mineral Belt area New Mexico, USA (Eadie C.G. and Kaufmann, R.F., 1977)	Uranium mining and milling activities evaluation of possible radioactive contamination of groundwater supplies due to ^{226}Ra, ^{230}Th, ^{210}Po.
2.	Geothermal waters in the Western United States (O'Connel M.F. and Kaufmann R.F., 1976)	Radiological evaluation of geothermal springs and wells for identifying potential environmental or health effects, following large scale development for energy, recreation, mineral recovery or agriculture.
3.	Brazilian mineral waters (Hainberger P.L., et al, 1974)	Radioactivity measurements for ^{226}Ra and ^{228}Ra activities in mineral waters from various parts of Brazil, to study natural activity levels.
4.	Florida, USA (Kaufmann R.F. and Bliss J.D. 1977)	West-Central Florida is a major centre of phosphate production in USA. Study aim was to relate Ra concentration in groundwaters with phosphate deposits, including their mining and processing activities.
5.	Florida, Sarasota (Kaufmann R.F. and Bliss J.D. 1977)	Extension of the same study as at No. 4 but the site location is at the extreme southern end of the Central Floridan phosphate district.
6.	Texas (Wukash M.C. and Cook L.W. 1972)	Uranium mining and milling region of South Texas; study of impact on ground water supplies.
7.	Australia. Yeelirrie, Western Australia.(Giles M.S., 1978)	Part of the baseline study in the environment of uranium deposits at Yeelirrie, Western Australia.

Table 3.2. Data Summary of ^{226}Ra Distribution in Ground Waters.

Parameter	Grants	Geothermal, Western USA	Brazil	Florida	Florida Sarasota	Texas	Australia Yeelirrie
Number of Values, (N)	72	136	268	246	49	24	53
Range (m Bq/l):							
Minimum	1.85	1.52	0.52	0	55.5	11.1	18.5
Maximum	1961.0	55500	3481.7	2812.0	902.8	6290.0	33374.0
Central Values: (m Bq/l)							
Median $\tilde{x}$	9.81	13.88	5.92	51.8	381.1	44.4	303.4
Geometric mean x_G	13.9	29.17	7.48	13.9	326.79	70.6	367.25
Arithmetic mean $\bar{x}$	57.4	870.97	78.85	98.03	406.02	679.4	2293.7
Confidence Intervals: (α=0.05) (m Bq/l) of the,							
Median	7.4- 13.69	9.99- 22.57	4.07- 7.4	44.4- 64.75	270.1- 458.8 (b)	(b)	133.2- 540.2
Geometric mean	10.12- 19.07	19.62- 43.4	5.91- 9.46	36.92- 51.16	265.78 401.8	31.56- 157.9	314.17- 629.7
Arithmetic mean	2.63- 112.18	20.86- 1721.08	34.29- 123.41	69.99- 129.30	335.6 476.5	45.79- 1404.6	759.5- 3827.9
Shape of Distribution:							
Skewness g_1	7.73043	9.91398	8.09973	8.41217	0.53867	2.5301	4.05694
Kurtosis g_2	63.48997	107.1287	71.341	88.09111	2.28209	7.80818	21.09286
Type of Distribution (a) :							
Normal	-	-	-	-	+	-	-
Lognormal	+	-	+	+ (c)	+	+	-

a) Analysis by Kolmogorov-Smirnov test, +: positive, -: negative
b) N $<$ 50, hence not reliable.
c) Calculated after omitting 4 zero values.

Table 3.3. Data Summary of ^{226}Ra Distribution in Surface Waters

Parameters	Brazil (Poços de Caldas)	Yugoslavia (Ziroski Vrh)	Australia (Northern Territory)
Number of Values, N	78	32	82
Range (m Bq/l)			
Minimum	7.4	0.37	3.33
Maximum	222.0	114.7	314.5
Central Values (m Bq/l)			
Median, $\tilde{x}$	7.4	1.48	27.56
Geometric Mean, x_G	14.52	1.91	29.22
Arithmetic Mean, $\bar{x}$	28.13	6.31	52.49
Confidence Intervals (α=0.05) (m Bq/l) for the			
Median	7.4-11.1	0.74-4.07	20.7-37.0
Geometric Mean	11.61-18.16	1.02-3.58	22.88-37.32
Arithmetic Mean	18.06-38.19	0.885-13.51	38.52-66.44
Shape of Distribution			
Skewness g_1	2.7822	5.2324	2.2920
Kurtosis g_2	10.2890	28.9367	8.6298
Type of Distribution (a)			
Normal	-	-	-
Lognormal	-	+	+

a) Analysis by Kolmogorov-Smirnov Test, +: positive, -: negative.

Table 3.4. ^{226}Ra Concentration in Stream Sediments

Area	Water (m Bq/l)	Sediment (m Bq/g)	Kd factor
Australia:			
Sawcut Creek	0.059	92.5	1.57×10^3
" "	0.0115	5.2	0.45×10^3
" "	0.0137	1.9	0.14×10^3
Georgetown Billabong	0.0481	15.5	0.32×10^3
"	0.130	4.4	0.034×10^3
"	0.034	16.7	0.49×10^3
India:			
Jaduguda, Juria nala, downstream of Uranium mill.	0.30	2038.0	6.8×10^3
"	0.11	784	7.1×10^3
Gara River bed, downstream	0.022	118	5.4×10^3

$$\text{Kd factor: } \frac{^{226}\text{Ra concn. in sediment (m Bq/g)}}{^{226}\text{Ra concn. in water (m Bq/l)}}$$

Table 3.5. Ra-226 Distribution in Fishes

S.No. (1)	Description (2)	Soft Tissue (Bq/kg) (3)	Bone (Bq/kg) (4)	Bone / SoftTissue (5)
BELGIUM:				
Fish from River Meuse				
1	Bream	7.62*	-	-
2	Barbel	1.77*	-	-
3	Trout	2.83*	-	-
INDIA:				
Jaduguda, Bihar:				
4	Catla Catla (Subarnarekha river)	0.2	12.95	64.8
5	Labeo rohita	0.019	0.55	28.9
6	" "	0.03	0.56	18.7
7	Fish (species not indicated) from mine water drains	2.96	51.8	17.5
8	" "	5.9	36.26	6.1
Alwaye, Kerala:				
9	Chana (ophiocephalus sp) upstream of industrial outfall area	0.074	0.703	9.5
10	Clupea longiceps Industrial outfall area	0.37	0.89	2.4
11	Etroplus Industrial outfall area	0.24	4.26	17.8
12	"	0.15	8.54	56.9
Kalpakkam, Tamil Nadu:				
13	Sole	0.079	0.55	7.0
14	Mackerel	0.17	-	-
15	Oil Sardine	0.19	0.91	4.8

* Eviscerated Whole

(3), (4), (5) relates to wet weights

Table 3.6. ^{226}Ra Distribution in Ophiocephalus sp.,

Jaduguda, India .

Catch No.	^{226}Ra Concentration (Bq/kg, wet)		Ratio $\frac{^{226}\text{Ra, in bone}}{^{226}\text{Ra,in muscle}}$	+Conc. Factor (CF)	
	Muscle	Bone		Muscle	Bone
1	2.59	20.57	7.9	5	40
2	6.0	36.18	6.0	11	70
3	5.59	33.85	6.1	11	65
4	7.92	39.77	5.0	15	77
5	7.51	37.77	5.0	15	72
6	5.55	34.11	6.1	11	66

+ A number of ^{226}Ra analyses of streamwater have given an average concentration of 0.518 Bq/l, on the basis of which the conc. factors have been derived.

Table 3.7. ^{226}Ra Distribution in Fish Muscle,

Australia.

Fish Species	Pre-mining data			Post-mining data		
	Tissue (Bq/kg, wet)	Water (Bq/l)	Concn. Factor (CF)	Tissue (Bq/kg, wet)	Water (Bq/l)	Concn. Fator (CF)
Barramundi	0.925	0.0136	68	4.44	0.0888	50
"	0.37	0.034	11	4.07	0.0063	646
"	0.185	0.01	19	0.37	0.0103	36
"	2.59	0.0074	350	0.37	0.0063	59
"	2.59	0.017	152	2.22	0.0089	249
"	8.51	0.1095	78	0.37	0.0063	59
"				0.74	0.0172	43
"				12.95	0.0294	440
Black Bream	2.96	0.041	72	3.33	0.0074	450
"	3.7	0.03	123	2.96	0.0405	73
"	-	-	-	3.7	0.0296	125

Table 3.8. ^{226}Ra Concentrations in Lake Water Fishes, *Perca Fluviatilis*, L., Italy.

Area/Sample	Ra-226 Concentration (Bq/l or Bq/kg (wet), Arithmetic mean and range	(Bq/g Ca^{+})	Conc. Factor (CF)
Lake maggiore			
Water	0.00052 (0.00019-0.00074)	0.027	
Fish	0.1184 (0.1073-0.1295)	0.0085	228
Lake Varese			
Water	0.00074 (0.0007-0.00078)	0.0226	
Fish	0.0518 (0.0481-0.0518)	0.0037	70
Lake Comambbio			
Water	0.00056 (0.00052-0.00056)	0.0218	
Fish	0.0777 (0.0629-0.0888)	0.0052	139
Lake monate			
Water	0.00052 (0.00044-0.00089)	0.0518	
Fish	0.0666 (0.03626-0.0814)	0.0044	128

$^{+}$ Ca concentrations are derived average concentrations of a number of Samples analysed by the authors.

Table 3.9. ^{226}Ra Concentration in Algae, *Spirogyra* sp. Jaduguda, India.

Location	^{226}Ra in Algae (Bq/kg, wet)	^{226}Ra in water (Bq/l)	Conc Factor
Tailings outfall Stream	8928.1	5.03	1.77×10^{3}
" "	7424.8	2.86	2.6×10^{3}
Mines stream	3169.8	1.22	2.6×10^{3}
Juria Nala 2km downstream of tailings outfall	2061.6	0.67	3.1×10^{3}
Gara Nala 2.7 km Downstream of tailings outfall	473.23	0.58	0.82×10^{3}
Gara Nala 3.25 km downstream of tailings outfall	251.23	0.11	2.3×10^{3}

Table 3.10 Ra-226 in Freshwater Mussels, Alligator Rivers, Australia

Location	Ra-226 Concentrations in Mussel (Bq/kg)	Water (Bq/l)	Conc. Factor (CF)
1-196535	12.2	0.0178	685
2-196486	2.6	0.0681	38
4-812269	165.8	0.0137	12100
3-680997	5.2	0.2257	23
3-599762	56.6	0.037	1530
3-599762	2.2	0.0096	230
3-599762	3.3	0.0389	85
3-752975	71.0	0.3127	227
3-752975	1.1	0.111	10
2-843924	18.1	0.0174	1040

Table 3.11 Ra-226 in Nearshore Marine Molluscs, Kalpakkam, India.

Description	Ra-226 Concentration in Molluscs (Bq/kg, wet)	Water (Bq/l)	Conc. Factor (CF)
Oyster, *Ostrea* sp.			
a) soft parts	0.08	0.0016	50
b) shell	0.80	0.0016	500
Green mussel *Perna viridis*			
a) soft parts	0.074	0.0016	46
b) shell	0.67	0.0016	419
Clam *Meretrix* sp.			
a) soft parts	ND	0.0056	-
b) shell	1.12	0.0056	200
Snail, *Thais* sp.			
a) soft parts	0.10	0.0016	63
b) shell	0.25	0.0016	156
Snail, *Petalla radiata*			
a) soft parts	0.07	0.0016	44
b) shell	0.41	0.0016	256

ND : Not Detected

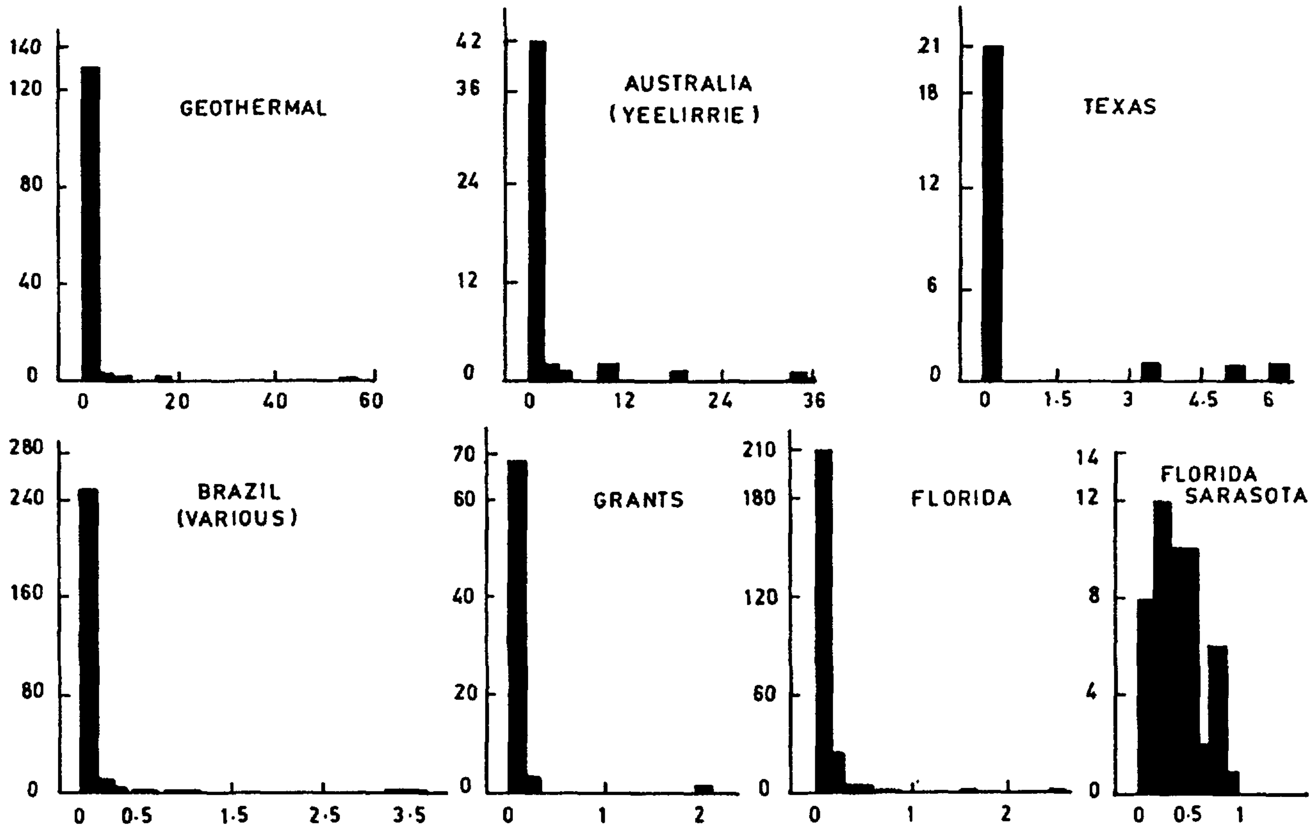

Fig. 3.1 Frequency distribution of Ra-226 in some ground-waters, [Geothermal (Western states, USA), Yeelirrie (Western Australia), Texas (USA), various sources (Brazil), Grants (New Mexico, USA), Florida (USA), Sarasota (Florida, USA)] (X axis = Ra-226 in Bq/l, Y axis = frequency in %).

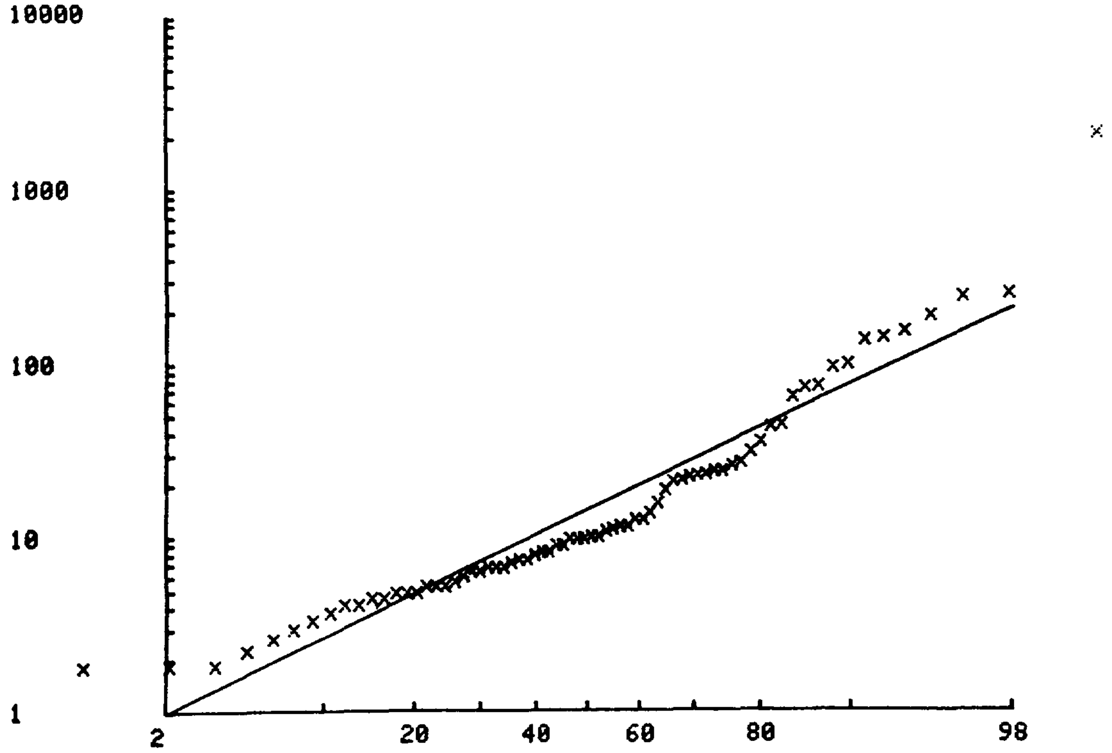

Fig. 3.2 Lognormal plot of Ra-226 concentrations relative in Grants groundwaters (New Mexico, USA) [X axis = relative frequency in %, Y axis = Ra-226 in mBq/l].

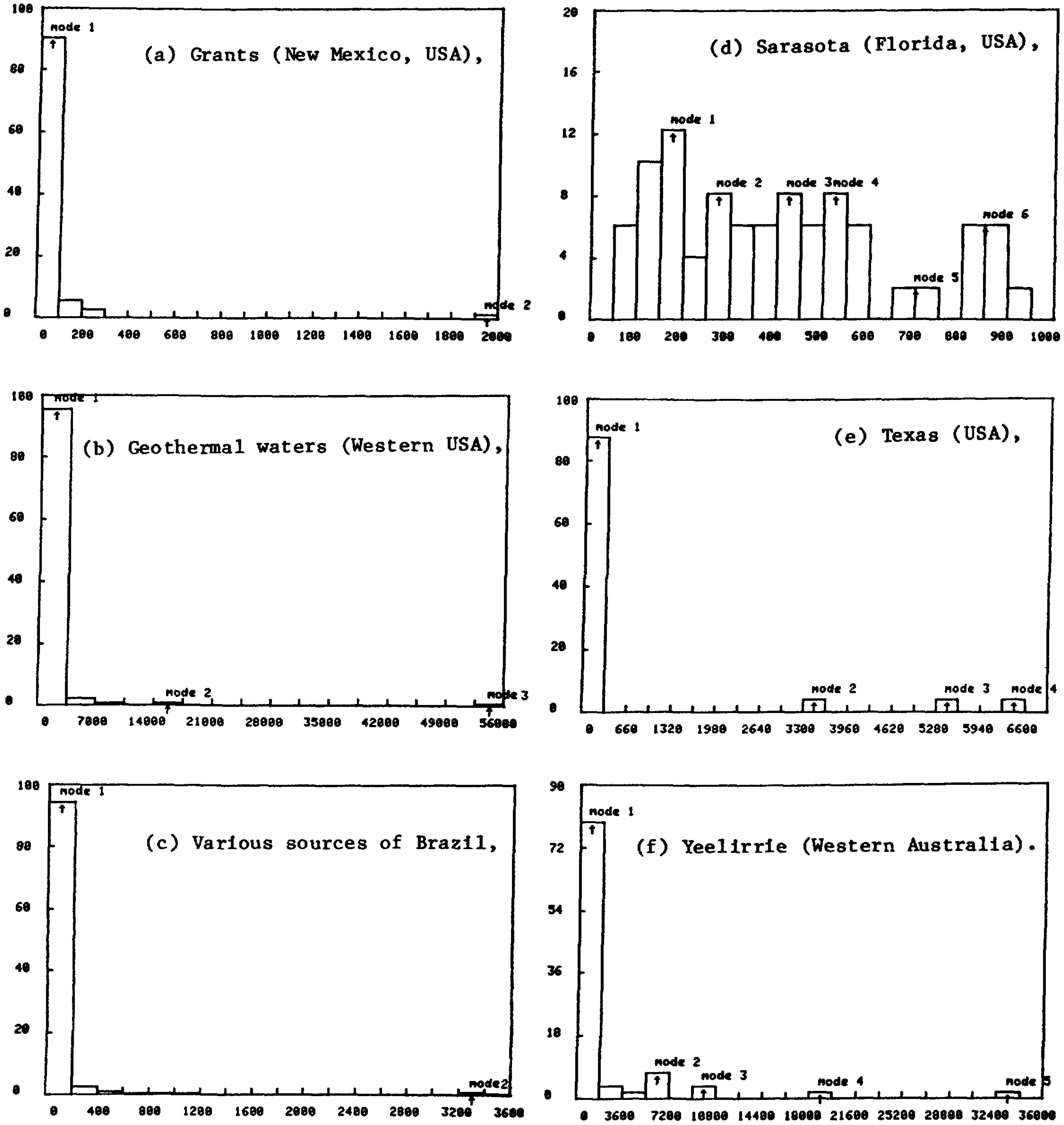

Fig. 3.3 Relative frequency distribution of Ra-226 concentrations in some groundwaters (X axis = Ra-226 in mBq/l, Y axis = relative frequency in %)

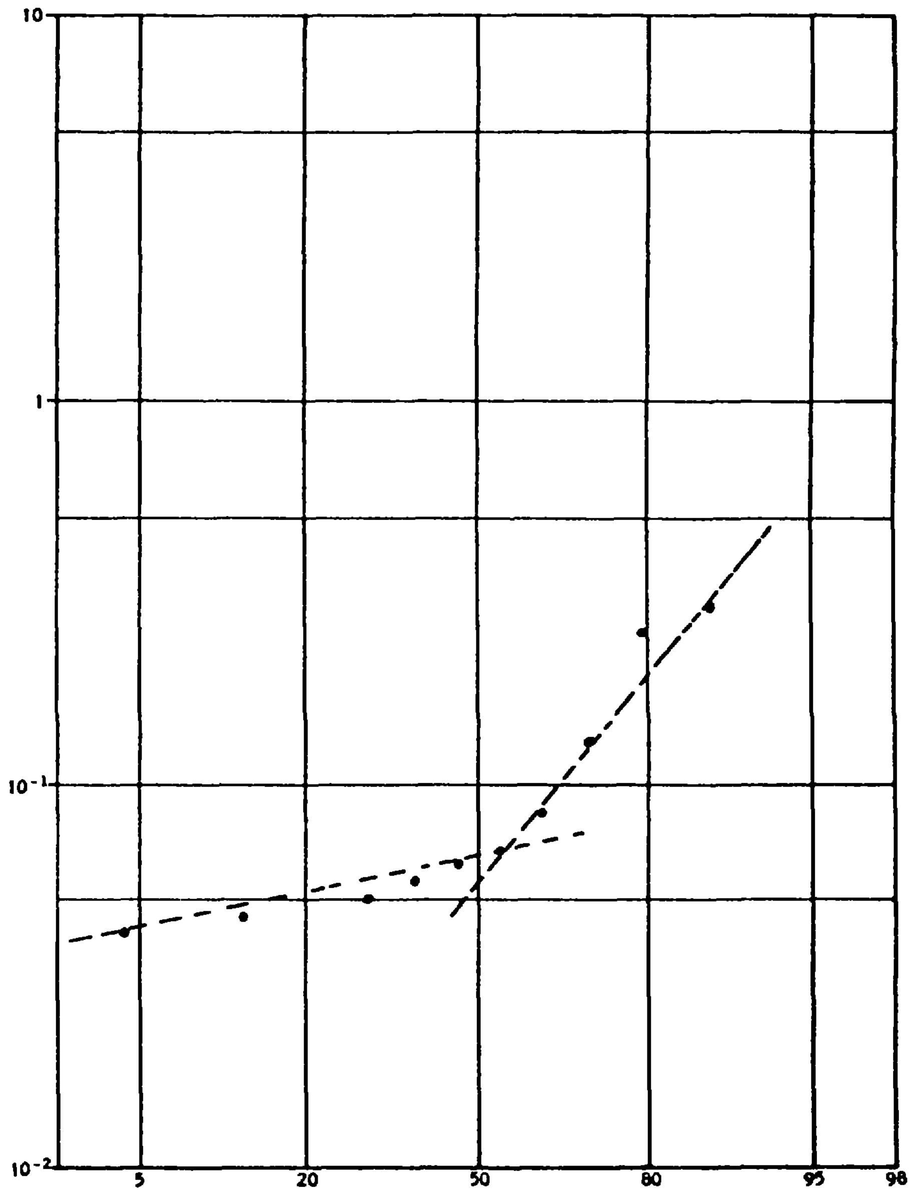

Fig. 3.4 Lognormal cumulative frequency distribution for Ra-226 in hot springs in Northern California, USA (from O'Connel M.F., Kaufmann R.F., 1976) [X axis = cumulative frequency in %, Y axis = Ra-226 in pCi/l].

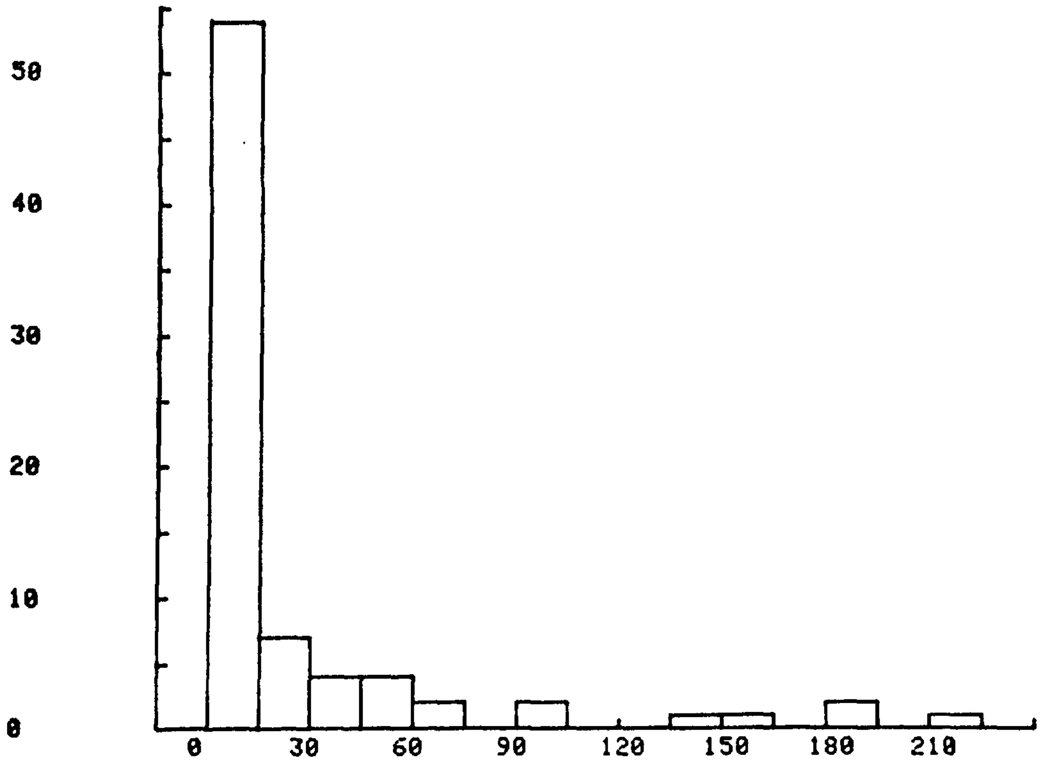

Fig. 3.5 Frequency distribution of Ra-226 concentrations in surface waters of Brazil (Poços de Caldas) [X axis = Ra-226 in mBq/l, Y axis = frequency in %].

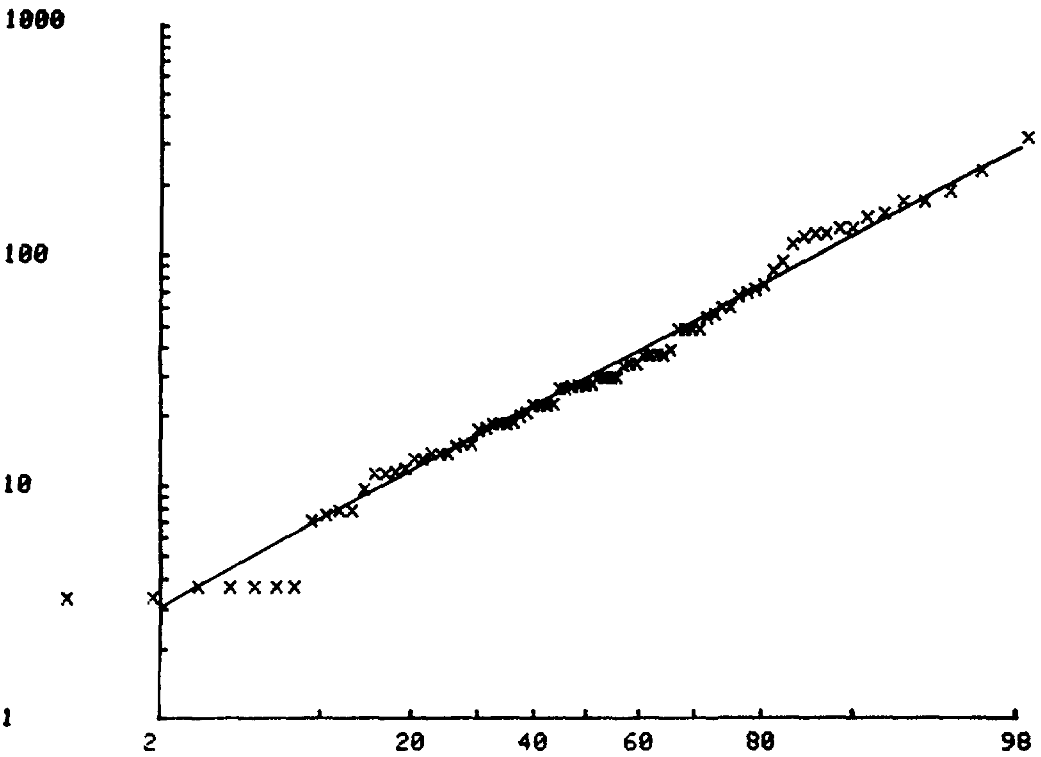

Fig. 3.6. Lognormal plot of Ra-226 concentrations in surface waters of Northern Territory in Australia [X axis = relative frequency in %, Y axis = Ra-226 in mBq/l].

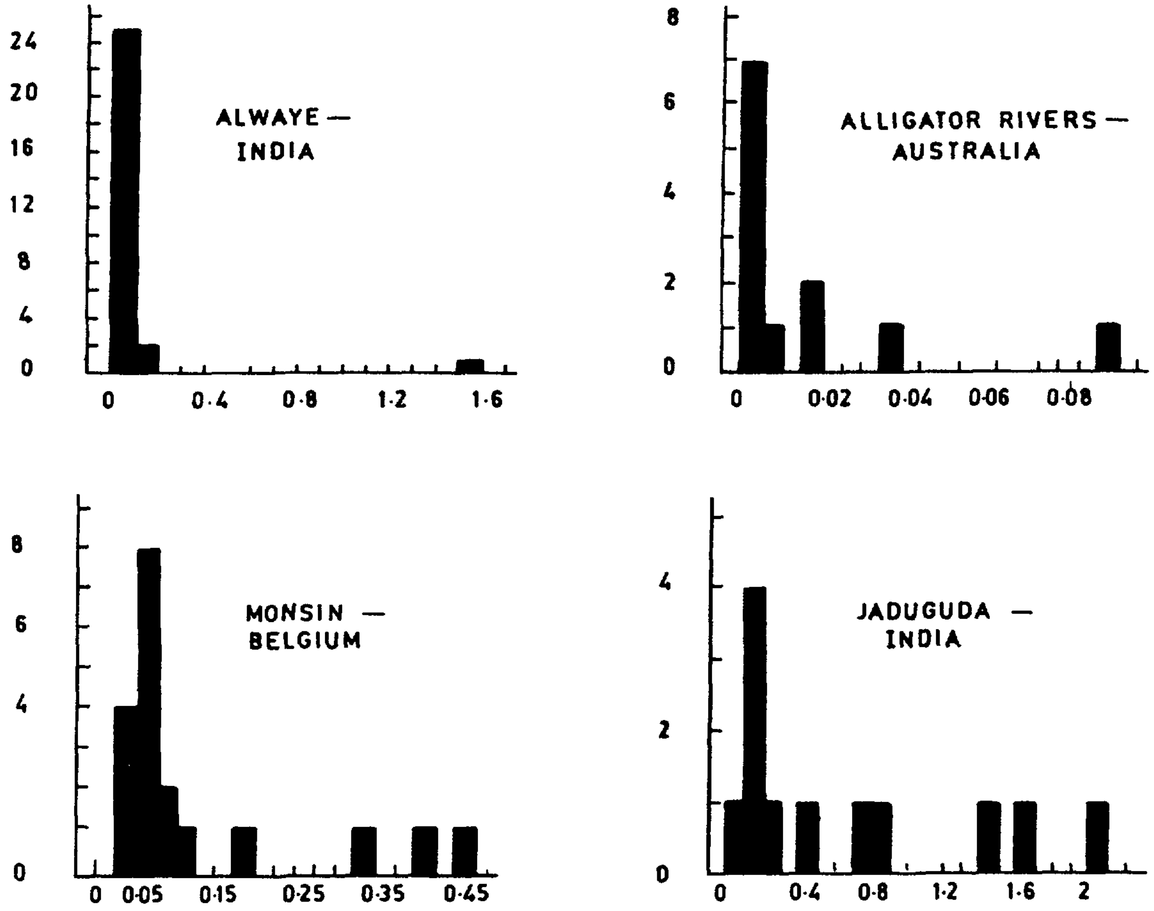

Fig. 3.7 Frequency distribution of Ra-226 in some stream sediments [X axis = Ra-226 in Bq/g, Y axis = frequency].

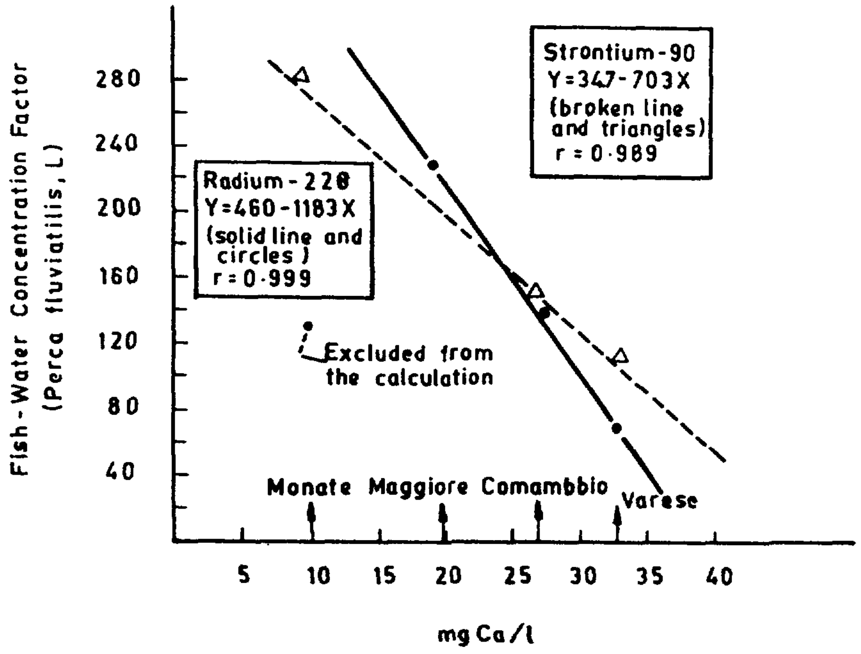

Fig. 3.8 Correlation between concentration factor of Ra-226 in fishes and Ca level in Italian lake waters (from De Bortoli M., Gaglione P., 1972).

REFERENCES

BROWNSCOMBE A.J., DAVY D.R., GILES M.S., WILLIAMS A.R., "Ground water quality in the general area of the Yeelirrie Uranium deposit", in Three Baseline Studies in the Environment of the Uranium Deposit at Yeelirrie, Western Australia, Australian Atomic Energy commission, Lucas Heights. AAEC/E442 (1978).

DAVY D.R. and CONWAY N.F., "Environmental Studies, Northern Territory Uranium Province in the Alligator Rivers Area, Fact Finding Study". Four AAEC reports, Australian atomic Energy Commission, Lucas Heights. AAEC/E305 (1974).

DAVY D.R., O'BRIEN B.G., "Radiological aspects in Rum Jungle environmental studies". (DAVY D.R., Ed) Australian Atomic Energy Commission, Lucas Heights, AAEC/E365 (1975).

DE BORTOLI M., GAGLIONE P., "^{226}Ra in environmental materials and foods". Health Physics, 22 (Jan) (1972) 43-48.

DENHAM D.H., WAITE D.A., "Some practical applications of the lognormal distribution for interpreting environmental data". 20th Annual Health Physics Society Meeting, July 14-15, 1975, Buffalo, New York pp. 31.

EADIE C.G., KAUFMANN R.F., "Radiological evaluation of the effects of uranium mining and milling operations on selected groundwater supplies in the Grants Mineral Belt, New Mexico". Health Physics 32, (1977) 231-241.

GAGLIONE P., MOLLER F., POLVANI C., Proc. Symp. International de Radioecologie Cadarache, France, September 8-12, (1969).

GILES M.S., "Groundwater quality in the general area of the Yeelirrie uranium deposit". in Three Baseline Studies in the Environment of the Uranium Deposit at Yeelirrie, Western Australia. (BROWNSCOMBE A.J., DAVY D.R., GILES M.S., WILLIAMS A.R., ed). Australian Atomic Energy Commission, Lucas Heights, AAEC/E442 (1978).

HAINBERGER P.L., DE OLIVEIRA PAIVA I.R., SALLES ANDRADE H.A., ZINDEL G., CULLEN T.L., "Radioactivity in Brazilian mineral waters". Radiation Data and Reports, 15, (1974) 483-488.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, Report of I.C.R.P. Committee II on Permissible Dose for Internal Radiation (1959). Publication 2. Pergamon Press.

IYENGAR M.A.R., MARKOSE P.M., "Monitoring of the aquatic environment in the neighbourhood of uranium mill at Jaduguda Bihar". Proc. National Symp. on Radiation Physics, Trombay, Bombay (1970) 473-484.

KAUFMANN R.F., BLISS J.D., "Effects of phosphate mineralisation and the phosphate industry on ^{226}Ra in ground water of Central Florida". Environmental Protection Agency, Las Vegas, USA (1977). EPA/520-6-77-010.

MIYAKE Y., SUGIMURA Y., TSUBOTA H., "Content of Uranium, Radium and Thorium in River Waters in Japan", in the Natural Radiation Environment, Rice University, Houston, USA (1964).

MITCHELL N.T., "Monitoring of the aquatic environment of the United Kingdom and its application to hazard assessment". (Proc. IAEA Seminar on Environmental Contamination by Radioactive Materials, March 24-28, 1969) IAEA, Vienna (1969).

O'CONNELL M.F., KAUFMANN R.F., "Radioactivity associated with geothermal waters in the Western United States: Basic data". U.S. Environmental Protection Agency, Las Vegas (1976) ORP/LV-75-8A.

PASCHOA A.S., BAPTISTA G.B., MONTENEGRO E.C., MIRANDA A.C., SIGAUD G.M., "^{226}Ra concentrations in the hydrographic basins near uranium mining and milling in Brazil". In Low level Radioactive Waste Management, Health Physics Society Symp. Williamsburg (1979).

PAUL A.C., LONDHE V.S., PILLAI K.C., "^{228}Ra and ^{226}Ra levels in a river environment and its modification by human activities". In the Natural Radiation environment III, Rice University Houston, USA (1978).

SANSONI B., IYER R.K., KURTH R., "Concentration of analytical data as part of data processing in trace element analysis". Fresenius Z. Anal. Chem. 306, (1981) 212-232.

TANNER A.B., "Physical and chemical control on distribution of ^{222}Rn in ground water near Great Salt Lake, Utah". In the Natural Radiation Environment, Rice University, Houston, USA (1964).

TSIVOGLOU E.C., "Environmental monitoring in the vicinity of Uranium mills". Proc. of IAEA Symp. on Radiological health and safety in mining and milling of nuclear materials Vol. II, August 26-31, 1963, Vienna (1964).

TSIVOGLOU E.C., O'CONNELL R.L., "Nature, volume and activity of uranium mill wastes", Proc. of IAEA Symp. on Radiological Health and Safety in Mining and Milling of Nuclear Materials Vol. II, August 26-31, 1963, Vienna (1964).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. Drinking Water Regulations (Radionuclides), Federal Register V. 41, No. 133, July 9, (1976), p. 28402-28409.

WUKASH M.C., COOK L.W., "Environmental Surveillance in South Texas". In the Natural Radiation environment II, Rice University, Houston, USA (1972).

Chapter 4

TECHNOLOGICAL ENHANCEMENT

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4.1. INTRODUCTION

One cubic metre of soil in somebody's backyard will contain on average 70 000 Bq of ^{226}Ra whereas the gold/uranium tailings dams spread over the highly populated area of the Witwatersrand, in South Africa, are estimated to contain some 2 500 TBq of ^{226}Ra. High as these figures may appear to be, put in the right perspective it will readily be seen that the former corresponds to 0.037 Bq/g, which is the mean radium concentration in the earth's crust, while the latter figure can also be expressed as 3 000 million tonnes of tailings with a mean radium concentration of 0.8 Bq/g. In one case one has the natural environmental situation where man has evolved since primordial times and in the other a more or less localised enhancement of radium brought about by man's technological activities.

Clearly, there are many sites of natural high radium concentrations such as hot springs and outcrops of uraniferous minerals, but the worldwide concern with the impact which radium may have on environmental waters is more specifically directed at activities concerned with the nuclear fuel cycle, particularly the front end, i.e. the mining and milling of uranium.

The expansion of the uranium industry since the fifties has necessarily given rise to a greater availability of radium capable of finding its way into surface and ground waters. With it came also a greater awareness, albeit slowly, of the potential impact which contamination of such waters could have on man, particularly because ^{226}Ra is the most restrictive nuclide amongst uranium daughters from a radiological point of view [1], considering the food-chain pathways.

Until not too long ago, the demand for ^{226}Ra, mainly for medical purposes, was such that in many processes where radium happened to be present as a secondary element it was economically advantageous to extract it. The picture has, however, changed drastically as radium has, in most applications, been superseded by more suitable radioisotopes. Radium is, therefore, considered as waste product to be disposed of on its own or in conjunction with other plant wastes.

Most investigations to date have, in the majority of countries, consisted of site-specific studies of relatively short duration, conducted during the operational phase and emphasizing the influence of surface discharge or subsurface seepage on water quality. Rarely are water,, soil, stream sediment and biological samples collected in the pre-operational period for radiological analysis. And even when this is done, assessment of risk due to technological enhancement is difficult because in most cases the difference between the natural radium levels in environmental waters and the slightly increased levels due to technological enhancement is relatively small. In the case of uranium mill tailings, for example, the volumes involved are usually large, so that the options available to adequately isolate the tailings dams from the environment over very long periods of time compatible with the half-lives of the radiosiotopes involved become limited. Thus, one of the greatest problems facing the uranium mining industry in general is that of control of radionuclides, particularly ^{226}Ra.

4.2. SOURCE TERM

Technologically enhanced contamination of surface and ground waters by radium is not exclusive to uranium mining. It occurs also as a result of mining for certain base metals such as copper (India, South Africa, USA) and tin (Cornwall, England); gold (South Africa); monazite ores and phosphatic minerals. Coals are also known to contain radium in various concentrations, which could lead to the ash residues discarded at power stations becoming enriched in radium.

The main sources of contamination of environmental waters are the following:

(i) Plant effluents
Generally, a portion of process waters enriched in dissolved and suspended materials is discharged to the environment.

(ii) Solid wastes
Leaching and/or seepage through the solid wastes can carry appreciable amounts of radium to the aqueous environment. Wind-blown dust is deposited over a considerable distance around the solid wastes impoundment but this is not considered to be a major contributor to the radium levels in water. Erosion could also be a problem, particularly in the long run.

4.2.1. Uranium

In underground uranium mining the solid wastes are deposited on the surface, either as waste rock piles, sand dumps or slimes dams. In the case of open-pit mining the same procedure is often used, although the trend in recent years, for hot and dry climates, is to refill the mined areas with waste material and cover it with the original top-soil. However, this procedure may not be suitable for some mined areas in subtropical regions, where the original mining sites become lakes unfitted to be filled with the original top soil.

Whereas past practices of tailings management were in many cases inadequate, serious efforts have been made during the last few years by private and public sectors as well as the IAEA to find ways to improve the design and management of tailings impoundments with the latest technology available, as reflected in pertinent symposia held recently [2, 3]. The general criterion has been to keep releases not only of radium but also of other detrimental substances as low as reasonably achievable.

4.2.2. Phosphates

^{226}Ra is known to occur in areas of phosphate mineralization as a result of the presence of uranium and its progeny. In the USA, for example, the concentration of natural radium in phosphate ore mined ranges from 0.2 to 10 Bq/g [4]. The most common method of beneficiation is by treating the mineral with sulphuric acid to produce phosphoric acid. Whereas most of the uranium remains with the phosphoric acid the radium and its daughters are discharged with the tailings.

4.2.3. Coal

Uranium and its daughter products are often present in coal in relatively low concentrations. While the coal remains unused there is usually little danger that radium will have any significant contribution to the contamination of environmental waters. However, during the combustion process the radium concentration will increase substantially as it follows the ash fraction. For this reason, concentrations of fly-ash, such as those which exist in the vicinity of conventional power stations, could constitute a significant source of pollution of environmental waters.

4.2.4. Others

Uranium and its decay products are known to occur fairly frequently as a by-product with minerals mined for their metal content. The relevance of such mining activities as a source of radium available for dissemination into the aqueous environment is essentially similar to the case of uranium mining: uranium concentration, hydrogeological factors and tailings management practices are the determinant factors. Plants used for the extraction of radium for commercial purposes, such as Hoboken, in Belgium, also have a considerable influence on radium concentration in environmental waters as a result of the effluents released. However, because this commercial activity has almost become obsolete, its future influence is expected to be small.

4.3. URANIUM MINING AND MILLING

The environmental pollution aspects of uranium mining and milling are to a certain extent similar to those of other metal mining operations. The unique feature lies on the emphasis that must be given to the radioactive releases experienced not only through the entire life of the mine but also for many years after cessation of operations. According to Swift et al [5], the solid tailings contain about 90% of all the radioactivity present in the original ore. The extracted uranium accounts for the other 10%. From that radioactivity, generally less than 1% of the radioactivity discharged from a uranium mill is in the tailings solutions, with 99% or more within the solids.

4.3.1. Economic Aspects

Analogous to management of nuclear power stations, releases of radium and other contaminants can be increasingly reduced at an ever increasing cost. This can be roughly quantified and the optimal point determined on a cost-benefit bases. The difficulty lies not only in adequately quantifying the health impact of low radium concentrations but also in establishing whether reduction of releases must be compatible with planning for hundreds or thousands of years. The long half-life of other radioisotopes in the tailings, such as ^{230}Th, makes control a long term problem. Furthermore, the radium which is recovered may create another problem of high-level waste disposal.

4.3.2. Acid vs. Alkaline Leaching

The two main methods used in the leaching process are acid and alkaline leaching. Whereas the former uses sulphuric acid and is rather non-selective in its leaching action, in the latter method a solution of sodium carbonate, sodium bicarbonate and an oxidizing agent to dissolve the uranium are employed.

Because the alkaline process is less violent, it requires greater comminution of the ore and the tailings contain therefore more fines [6]. Also, because the process is carried out at pH 10-11 there are fewer mobile constituents. In the case of acid leaching (pH 1.7 - 2.0) much of the radium and other elements present in the original ore are dissolved in the effluent but will eventually interact with the soil and water under different pH conditions and precipitate or adsorb onto the surface of soil particles.

4.3.3. Underground vs. Open-Pit Mining

From the point of view of radium impact on environmental waters, the two methods differ chiefly on the way tailings are disposed of. In underground mining the tailings are piled above ground level, albeit in locations carefully chosen after topographical, geological and hydrogeological studies. Such tailings dams are nevertheless exposed to wind erosion, possibility of catastrophic failure and sheet run-off. In open-pit mining these effects are practically eliminated if the depleted pits are used for disposal of the tailings, but the problem of seepage could be considerably more relevant than in the case of tailings piles. This is particularly true when the bottom of the pit is situated below the regional water table. Clay liners can be used to limit seepage but the fact remains that very little is known about the impact of such type of disposal on underground water [7].

4.3.4. Climatological Considerations

The type of climate prevailing in a specific uranium mining area determines the nature of the impact which the radium contained in the liquid and solid wastes will have on the environment. If the climate is dry, as in New Mexico and on the Witwatersrand, most of the water discharged onto the tailings dams will evaporate, resulting in drying out of the tailings and radon will be the radionuclide of concern. In wet climates, such as that of Canada, there will be relatively little radon escape but radium will very likely find its way into surface and ground waters.

4.3.5. Site-Specific Aspects

Every ore deposit or tailings dam has its own peculiarities in terms of associated uranium grade and mineral composition, permeability and sorption capacity, relation to the water table, and physical, chemical and hydrogeological properties of the underlying soil. Therefore, situations which at a first glance may appear similar could have the radium behaving in quite different ways. Also, for a given radium concentration in environmental waters the importance of the net impact is largely dependent on population distribution as well a land and water usage in the area.

4.3.6. Tailings and effluents

Uranium tailings are essentially the same material as the original ore mineralization, with two exceptions: a large surface area is produced as a result of grinding and most of their uranium has been extracted by chemical treatment. Acid tailings are usually neutralized by lime addition before they are deposited in piles (tailings dams) formed from a slurry containing anything up to 80-90% water. The dams consist of interbedded layers of materials ranging from clay to coarse sand in texture. The neutralization causes the precipitation of a large portion of the radium and many of the dissolved salts and metals. The net result is that most of the radium from the ores appears in the tailings [8]. However, there is good reason to doubt whether liming will be of much benefit on the long-term when sulphides are present [9]. Liming is only a short-term measure and eventually the aciditiy resulting from the oxidation of the sulphides will be the determining factor in the creation of a low pH environment which could result in serious leaching problems.

The liquid wastes usually have their pH adjusted but this alone does not necessarily reduce the radium concentration to acceptable levels. Thus, they are often subsequently treated with flocculants [10] to precipitate the suspended radium and/or with barium chloride to precipitate the soluble radium before they are released to surface and ground water (see Ch. 8).

4.4. Ra-226 DISTRIBUTION IN THE AQUEOUS ENVIRONMENT

Perhaps spurred by the potential health hazard inherent to radium contamination of the environment caused by uranium mining and milling, several countries are making a larger effort in terms of studies, surveys and monitoring programmes aimed at assessing the size and nature of the impact which radium is having on environmental waters. In what follows the most important findings concerning technologically enhanced concentration levels of ^{226}Ra in waters will be described. For the sake of clarity, the results obtained at each site will be grouped under the headings "ground water", "surface water", "stream sediment" and "biota". Sites in the following regions have been investigated:

Alligator Rivers and Yeelirrie regions, Australia.
Mining has not yet started but an extensive pre-operational impact study has been carried out [11]. Ore grade ranges from 1300 to 18 000 g/t U_3O_8.

Olen and Tessenderlo, Belgium.
Regions housing a radium extraction plant and factory where natural phosphates are treated, respectively.

Northern Bohemia, Czechoslovakia.
Uranium mine situated in region of high natural radium concentration (25% of water supplies and wells measured by Martinec and Havlik [12] contained more than 0.12 Bq/l ^{226}Ra).

La Crouzille, Vendée and Forez, France.
Three regions where uranium is mined and milled.

Jaduguda and Alwaye, India.
Jaduguda has the oldest uranium mine in India and Alwaye a monazite and a rock phosphate processing plant.

Tono mine, Japan.
Mining and milling or uranium is undertaken.

Witwatersrand, South Africa.
A few dozen gold/uranium mines are intermingled with highly populated urban areas.

Grants Mineral Belt, North Carolina and Florida regions, USA.
The Grants Mineral Belt includes several uranium mines spread over a sparsely populated area, while uranium-bearing phosphate ore is mined in North Carolina and Florida.

Pocos de Caldas, Brazil.
Mining area and future milling facilities are planned [26].

Yugoslavia.
There are two sources of radium pollution, namely an exploratory uranium mine of Zirovok vrh, a phosphate mill and a coal separation plant at Zasavje.

4.4.1. Ground Water

4.4.1.1. Mechanisms of contamination of ground waters

Technologically enhanced contamination of ground waters by radium takes place as a result of leaching of waste materials by rain water or as a result of seepage of already contaminated surface waters flowing over or contained in permeable soils. Seepage of rain water falling on contaminated ground or sediments will, obviously, also lead to enhanced radium concentrations in the ground water. However, uranium tailings impoundments, owing to the relatively large total amounts of radium which they contain, are perhaps the most significant single contributors to the enhanced radium levels in ground water. Even when a tailings dam is decommissioned, seepage into the underlying soil could continue for many years [13], the quantity of seepage release being dependent not only on the seepage control system but also on the properties of the foundation soil or rock beneath the impoundment and the nature of the ground water in the area. According to Klute et al [14], the general sequence of water-flow events may be described as follows:

1. An initial period of drainage from complete saturation, with evaporation at the surface;
2. Infiltration of various amounts of rain at regular intervals; and
3. Periods of evaporation and drainage from the profile and redistribution of water within the profile between rainfall events.

The same author further maintains that the initial drainage from saturation, if not disturbed by rainfall events, could last for several years., This opinion is supported by that of other workers [13].

4.4.1.2. Specific site studies

Ground water concentrations of radium in areas included in this study are as follows:

(a) Yeelirrie

The natural ^{226}Ra concentration of underground water can be as high as 30 Bq/l. However, owing to the low rainfall (200 mm/a) and the relatively high level of natural contaminants in ground water the environmental impact of mining is expected to be small [11].

(b) Olen and Tessenderlo

No specific study of ground waters was conducted but it was established that ^{226}Ra dissolved in water from domestic wells and bore-holes drilled in an area contaminated by liquid effluents was, in most cases, below 0.37 Bq/l [15].

(c) Jaduguda

The uranium mine at Jaduguda has ore of fairly low grade but has been in operation for many years. A brief survey, conducted already in the late sixties, of several wells in and around the mine premises whose water is used for domestic purposes, gave concentration levels which varied between 0.16 and 0.02 Bq/l ^{226}Ra. No conclusion regarding the possibility of contamination could be made. A subsequent and more comprehensive survey carried out over four years, produced more meaningful results. These are shown in Table 4.1. In the case of both wells, it may clearly be seen that while the Cl^-, $SO_4^=$ and Mn levels have increased considerably over the four years, there has hardly been any movement of radium. A further interesting aspect is that there are no significant differences between the values found for the well adjacent to the tailings pond and those for the well 500 m away. Dispersion considerations would have led one to expect a lower concentration in the latter if the seepage originates in the tailings pond itself. The values obtained are those that might be expected from seepage through contaminated upperlying soil.

(d) Witwatersrand

A similar situation of low radium mobility seems to exist at least in one of the South African gold/uranium mines situated in a dolomitic area. The tailings impoundment is about 25 years old. In spite of the high sulphate and manganese levels recently measured in ground water at approximately 1 km from the impoundment, the radium concentration levels in several boreholes located hydraulically down gradient from the impoundment never exceeded 0.03 Bq/l of dissolved radium. Unfortunately the data available are still too few to draw any meaningful conclusions.

(e) Grants Mineral Belt, North Carolina and Florida

Several studies concerning the effects of uranium mining on ground waters have been conducted in the USA [7, 16, 18], particularly in the State of New Mexico where, due to the scarcity of perennial surface water bodies, ground water is the main source of water in the mining areas. Industrial, municipal, stock and private domestic wells tap both bedrock and aluvial aquifers [7].

(i) Grants Mineral Belt

Although previously there had not been much interest in ground water contamination, subsequent investigations in the Grants Mineral Belt involved sampling 72 wells and various mine drainages in the area, review of hydrogeological conditions and a check of water balances for two tailings pond complexes [17]. The study revealed that from the 72 ground water sampling locations, seven locations showed dissolved ^{226}Ra concentrations above the 0.12 Bq/l drinking water standard used in the USA. However, only two potable water supplies contained ^{226}Ra in excess of the water standard. Concentrations in municipal water supplies varied between 0.005 and 0.025 Bq/l. Lack of pre-operational data failed to indicate whether the higher radium concentrations are due to mining.

Seepage from the Anaconda mill tailings pond alone averages 183 million litres per year and enter an aquifer used for domestic and irrigation purposes. On this basis it is estimated that between 1960 and 1970 about 15 GBq of radium were introduced into the aquifer through seepage alone. At the Kerr-Mcgee mill some 30% of the wastes channelled into the evaporation ponds escape by seepage. Although nearby wells revealed high levels of ammonia and nitrate the maximum radium concentration observed was 0.24 Bq/l. An estimated 30 GBq of radium has been introduced into ground waters in this area. Again, lack of "true" background or ambient values prior to uranium mining make adequate evaluation of radium enhancement well-nigh impossible.

Whether mines in the Grants Mineral Belt region contaminate ground waters by means of ground water leaching or by recharge through contacting exposed oxidised ore bodies is poorly documented.

Preliminary studies by the US Geological Survey indicate good quality water from one inactive underground mine in the Churchrock area and it may well be that this water could be considered as sufficiently potable to be used as municipal water supply.

Because of the co-location of mining and milling facilities in New Mexico it is difficult to identify impacts from one versus the other. A monitoring well network to determine temporal and spatial trends in ground water has nevertheless been installed.

(ii) North Carolina

A study carried out by Strain et al [4] around a phosphate mining and manufacturing facility in North Carolina revealed that although four wells had dissolved ^{226}Ra concentrations ranging from 0.35 to 5.5 Bq/l most of the remaining 22 wells had concentrations below 0.074 Bq/l. Perhaps interesting is that another well situated no more than 40 m from that containing 5.5 Bq/l gave a ^{226}Ra value of only 0.044 Bq/l. Their radon concentrations were 700 and 12 Bq/l, respectively. Water from many of the wells has been used by residents for domestic purposes and, according to the authors, continuous intake of water from the well with a radon concentration of 700 Bq/l would result in a dose equivalent rate to the stomach of 20 mSv/y. The equilibrium bone burden from the ^{226}Ra would correspond to a dose equivalent of about 48 mSv/y.

(iii) Central Florida

Kaufmann and Bliss [19] studied the effects of phosphate mining in Central Florida on ^{226}Ra contents of ground water and concluded that there was no difference in the radium content in the water table aquifer in mined and non-mined mineralized areas when compared with that in non-mineralized areas. They concluded, therefore, that mining as well as mineralization have not given rise to widespread and/or significant increases in the radium content of such an aquifer. Dissolved radium concentrations in the discharges ranged from 0.0008 to 0.08 Bq/l and total radium never exceeded 0.12 Bq/l at any one facility. It is, however, presumed that seepage to ground water could contain higher total radium, depending on the transport route and the suspended solids content of the waste water. The mean radium concentration dissolved in ground water for the area studied gave averages ranging from 55 to 550 Bq/l, most of it originating from the high natural levels of radium prevailing in the area.

In mining areas where the natural concentrations of radium are of the same order of magnitude of those corresponding to the limits set for the public, the capacity to absorb additional quantities is sometimes almost nil. Under such circumstances there is a serious problem in how to dispose of the radioactive wastes during mineral extraction of ores having uranium associated with them.

4.4.1.3. Comments

From the above studies it is not clear that technological enhancement was responsible for the higher radium values found in ground waters as little background data is available.

4.4.2. Surface Waters

4.4.2.1. Mechanisms of contamination of surface waters

Most of the radium enhancement in surface waters seems to be caused by discharge of mine and milling effluents into watercourses. Other possible causes are wind and water erosion of tailings dams, occasional flood waters from mill areas and seepage water from tailings impoundments, which may conceivably reach the surface through open fountains. However, their contribution must be regarded as minor in comparison with that by effluents discharged.

Treatment of the effluents by barium chloride has the effect of removing most of the dissolved radium by precipitation. However, if the mean residence times of the treated effluents in the settling ponds is not sufficiently long to allow the radium to settle, large quantities of radium in the form of fine suspended material may still be released into the environment and be eventually deposited as sediment.

The ratio of dissolved to suspended radium in the effluents depends on their history and previous treatment. From the time they are released to any stream or aquifer the further behaviour of radium is influenced by various factors, the effects of which are not yet fully understood. Some of the most important are pH, type and concentration of ions, dilution factors, oxidation potential of the water medium as well as chemico-physical composition and hydrogeological properties of the river/resorvoir bed and underlying soil. Their influence is subject to appreciable changes caused mainly by seasonal variations in the behaviour of surface waters.

The impact which radium in surface waters may have on a specific environment depends on how that environment relates to man. Such waters are usually more accessible to man and other biological systems and, in the case of rivers, can lead to widespread contamination of adjacent areas. The majority of countries involved in uranium mining are also actively involved in studies, surveys and monitoring programmes designed to gather information on and to learn more about the behaviour of radium in surface waters. In most cases, however, those steps have been taken only after mining and milling had been in operation for several years.

4.4.2.2. Specific-Site Studies

The following ^{226}Ra concentrations in surface waters have been found in this study:

(a) Alligator Rivers region

This region is a wilderness area of great natural beauty, which is intended for a major natural park. Practically all ore bodies are to be mined by open-pit. The average rainfall of the region is 1300 mm while evaporation is about 2200 mm. Except for one mine, all uranium development plans envisage no release of contaminated waters [11]. Only 0.1-0.3% of the radium will be released into solution and its concentration in waste liquours after lime treatment is expected to be 0.1-0.5 Bq/l. In order to keep the annual radium intake by the local population under the limit of 300 MBq, the allowable increase in the radium concentration of a local creek used by the aboriginal population will not be higher than 0.02 Bq/l.

(b) Olen and Tessenderlo

As part of a survey carried out in an area contaminated by ^{226}Ra in the effluents of a radium processing plant, the concentration in dissolved and suspended ^{226}Ra in the stream into which the effluents were discharged was measured [15]. The authors found that the total ^{226}Ra concentration in the stream water tended to increase downstream at least over a distance of approximately 1.5 km. The concentration increased from 0.075-0.4 Bq/l to 0.022-0.81 Bq/l. The cause for these variations is not clear, particularly considering that the second measuring point was in a zone of drainage canals, with practically no horizontal movement of the waters. What they have further verified is that in spite of the lack of turbulance in this zone, the activity due to the radium adsorbed onto suspended matter was considerably higher than that due to dissolved radium. They found no correlation between the appreciable variations in the ratio solid/suspended radium and the pH or Ca^{++} concentration. They also observed an increase in the concentration of soluble radium at the point where the stream joins the river and this they attribute to the possibility of elution taking place.

Measurements carried out by the same workers in the Tessenderlo region, have shown that the effluents from the phosphate plant discharged into two rivers gave rise to dissolved radium concentrations as high as 0.4 and 1.0 Bq/l, respectively. In contrast with the Olen region, in this case most of the radium seems to be present in dissolved form.

(c) Northern Bohemia

Radium contamination of surface waters in the uranium mining area studied results mainly from two sources of waste water: drilling waters, which are pumped out of aquatic sandstones around the mine, and mine waters, which are pumped out directly from the mine. Their ^{226}Ra content varies and it can be as high as 37 Bq/l. While most of the radium content in drilling waters is in solution (about 97%), that in mine waters shows a greater abundance of the suspended form (between 3% and 35%). Assessment of the effect of mining on the radium content of surface waters has been made possible because data corresponding to the period prior to the start of uranium mining is available. These data have been reported elsewhere [20, 21].

The situation concerning radium concentrations in surface waters is illustrated in Fig. 4.1 and Tables 4.2 and and 4.3. Table 4.2, which refers to the outlet of effluents from the sedimentation pond, clearly shows large non-seasonal fluctuations in the total amount as well as in the forms of radium released to the Ploucnice river. The percentage of dissolved radium is in all cases quite small. Releases of 5.5 Bq/l ^{226}Ra (Table 4.3) led to concentrations of 1.5 Bq/l in the river just after the release point and 0.86 Bq/l 12 km further downstream, most of it still in the suspended form.

(d) La Crouzille, Vendée and Forez

The liquid effluents from the uranium mills, after sedimentation in the settling ponds, can have radium concentrations well above 10 Bq per litre. A radium balance carried out over several years in the Vendée region has shown that 1% of the radium entering the mill is released as dissolved radium. In Table 4.4 the quantities released during 1975 in the La Crouzille, Vendée and Forez regions are compared with the soluble radium concentration in the respective receiving rivers. It may clearly be seen that the enhanced radium concentration due to mining is indeed small.

The dilution of the effluents in the rivers varies from a factor 2 to 10 depending on the size of the rivers. The ratio of insoluble to soluble radium contents in one of the rivers was found to vary between 1.4 and 3.2 and to decrease with distance due to dilution and sedimentation. For example 15 km downstream the ratio was 0.6, which is very similar to the ratio of 0.5 that prevails upstream from the release point.

(e) Jaduguda and Alwaye

The natural radium dissolved in surface waters in the Jaduguda region, as measured before the start of mining activities, ranged from trace levels to 0.07 Bq/l. Measurements conducted during 1977/78 have revealed that the concentration of dissolved ^{226}Ra in the Juria Nala river at a point just after the release of the effluents from the tailings pond average 1.7 Bq/l, reached a maximum of 2.4 Bq/l at about 1.5 km further downstream, where the Juria Nala meets the Gara Nala river. At 6 km downstream from the release point the average radium concentration has come down to 0.03 Bq/l. As in the case of wells, the local population makes intensive use of water from both rivers for domestic consumption. Measurements carried out at three different times of the year, monsoon season, late winter and summer, have shown that during the monsoon season the radium concentration levels are considerably diluted by the heavy water-flow.

The liquid effluents from the monazite processing plant in the Alwaye region are discharged into the Palar river. To study the impact of this industrial activity on the river water, the river was divided into three zones. These are given below, together with the dissolved radium (^{226}Ra, ^{228}Ra) concentrations measured.

(i) Background zone - where impact of industrial operations is not considered significant.
Dissolved radium: 0.002 - 0.122 Bq/l
Suspended radium: 0.02 - 0.190 Bq/l

(ii) Industrial zone - where the river is directly subjected to industrial effluents.
Dissolved radium: 0.002 - 0.089 Bq/l
Suspended radium: 0.096 - 2.7 Bq/l

(iii) Backwater zone - downstream from industrial zone and in close proximity to the sea.
Dissolved radium: 0.005 - 0.026 Bq/l
Suspended radium: 0.089 - 7.2 Bq/l

No discernable enhancement of dissolved radium has been noticed, albeit the concentrations of suspended radium in the industrial and backwater zones have increased appreciably.

(f) Tono uranium mine

The mine has been in operation since 1974 and in-place leaching is used. Measurements carried out regularly show not only an extremely low radium concentration in the effluents from the precipitation pond but also a continuous decrease in mean concentrations between 1974 and 1977, as may be seen from Table 4.5. These concentrations are of the same order or perhaps even lower than those measured in river and well waters.

In order to investigate the general behaviour of radium in river water, a river fed by a hot spring was selected as model. Through measurements of the concentration of $SO_4^=$ Cl^-, Fe, Mn, and ^{226}Ra at various points along the river and a mass balance exercise the conclusion was drawn that depletion or enhancement of ratios such Ra/Cl would reflect the behaviour of radium along the stream in terms of its deposition or re-dissolution.

(g) Witwatersrand

A preliminary survey of environmental surface waters was conducted in the gold/uranium mining areas, particularly in those areas which have either a high population density or are intensively cultivated. The measured total radium concentration in rivers, dams and lakes with free access to the public are shown in Table 4.6, from where it may readily be seen that concentration levels of total ^{226}Ra in environmental waters seem to be remarkably low, particularly considering that there are some 2500 TBq of ^{226}Ra contained in the tailings impoundments spread throughout the area. The only high value (1163 Bq/l), at the Rietspruit site, is caused by the liquid effluents discharged by a uranium mill situated some 5 km upstream. It is regrettable that no data on natural radium concentrations are available but this is understandable if it is realised that mining activities in many of the areas surveyed have continued uninterruptedly since the turn of the century. The 0.11 Bq/l measured in the Nigel Dam site results from the fact that this lake used to receive some of the effluents from a mine. Its outlet flows through a town for almost 2 km and at the end of this distance the radium concentration had dropped to only 0.092 Bq/l.

(h) Grants Mineral Belt and North Carolina regions

In the Grants Mineral Belt most of the uranium mills discharge their liquid effluents into streams after barium chloride treatment. Those with no discharge utilise evaporation ponds or use the water for dust control. In some mines and milling sites the water volume of streams into which mine effluents are discharged decreases consistently with flow distance but water quality changes are erratic. Infiltration can account for 90% or more of the water lost, the balance being by evaporation. One case was observed where dissolved ^{226}Ra decreased from 0.52 to 0.035 Bq/l over a distance of 27 km. Based on the limited flow and other measurements concerning water quality, it appears that radium is strongly sorbed onto the stream sediments. This type of studies have led to the conclusion that ^{226}Ra is removed from surface waters at rates of 0.02 to 0.11 Bq/l per kilometre of stream. Final concentrations are of the order of 0.009 Bq/l. Redissolution in successive surface flows seems to occur but not significantly.

It has also been observed that water pumped from the mines has some impact on shallow ground water in alluvial aquifers although this is not properly documented. It would appear that most of the mine effluent infiltrates within short distances and recharges the shallow water table. The dissolved, generally non-reactive contaminants such as chloride and sulphate are expected to reach the water table, but reactive contaminants such as radium and most trace metals would sorb or precipitate in the soil in the course of infiltration. Although no cases of gross, widespread contamination of surface waters seem to have been found in the Grants Mineral Belt there are some cases of local contamination of water.

At the North Carolina phosphate plant the overflow of the settling pond is dispersed into the Pamlic river. Although the dissolved radium concentration in the river water was less than 0.02 Bq/l, the mean concentration downstream from the plant was consistently higher than upstream, i.e. 0.01 an 0.005 Bq/l, respectively.

(i) Zirkovski vrh region

Measurements conducted in 1977 on the Brebovscica river before full-scale uranium mining operations started show the radium concentrations of dissolved ^{226}Ra to have increased from a mean of 0.002 Bq/l to approximately 0.006 Bq/l in the vicinity of the point where effluents are discharged. The radium contents of the effluents ranged between 0.037 and 1.8 Bq/l. Further measurements conducted in the Sava river, which has the Brebovscica as one of its tributaries, showed no contamination caused by the mining activities as such. What appears to have had a slight contribution to the radium content of the Sava are the liquid effluents from a phosphate mill and coal separation plant situated some 80 km downstream from the uranium mine.

4.4.2.3. Comments

In spite of insufficient information regarding radium concentrations in surface waters prior to starting of mining or milling operations there is, in a few cases, clear evidence of radium enhancement caused by such activities.

4.4.3. Stream Sediment

4.4.3.1. Mechanisms of transfer through sediments

The behaviour of the radium discharged into a river is strongly influenced by the organic and inorganic substances already present in the river and in the effluent itself. If the pH of the effluent is of the order of 6 to 7, as is often the case, when the effluents mix with river water the pH is usually increased and this leads to the precipitation of hydroxides of Fe, Al and Mn. The radium precipitates with these hydroxides as well as with the sulphates which are present, in particular those of barium. The presence of plant life will enhance retention of the hydroxide particles by capturing them.

Further downstream, part of the contamination of bottom sediments can be attributed to fixation of the radium onto clay particles. Where streams are slow moving, the deposition of fine particles is favoured. In the same zone, the sedimentation of organic debris enriches the deposit of organic matter on the river bed and the resulting consumption of the available oxygen can give rise to reduction of sulphates to sulphides.

During seasonal floods radium attached to the sediments can be redissolved and redeposited again, often over long distances, once favourable conditions are reached. If the river overflows its banks radium-carrying sediments may be deposited onto the flooded areas. Heavy rains can cause tailings material, which is often spread in the vicinity of tailings impoundments, to be carried into a receiving stream.

4.4.3.2. Specific site studies

(a) Olen and Tessenderlo

The main purpose of the study [15] conducted in this area had been to establish whether the effluents discharged into streams which periodically overflowed their banks had led to contamination of soil being considered for agricultural purposes. The study revealed that the top layer of soil, consisting mainly of turf, was highly contaminated by radium. An area of 0.66 ha gave values of 37 Bq/g ^{226}Ra while in some 9 ha the concentration levels ranged from 3.7 to 37 Bq/g. According to the authors "the degree of adsorption of the radium onto the turf is such that its migration is extremely limited and the present situation will hardly change within several centuries".

(b) Northern Bohemia

Stream sediment in the mining area as well as along the Ploucnice river were investigated in 1977 and again in 1979 for their radium content. From the results in Table 4.7 (1979 study) it can be seen that the radium content decreases significantly as the distance from the source of radium increases. The only exception to this regular decrease in radium at one of the sampling sites can be explained by the higher abundance of the "fine" fraction at this site. The regular decrease is caused by the rapid sedimentation of suspended forms of radium and by mixing of radioactive sediments with an increasing portion of sediments of low radioactivity. It further follows from the data in Table 4.7 that the fine particles of the sediments contain the largest portion of the radium. A good correlation was found between the radium content of the sediment and that of water, specially as regards the particulate form. The relatively small reduction in weight after ignition shows that very little organic material was present in the sediments. Comparison of these results with those obtained during an earlier study showed that there has been an increase in the content of radium in the sediments during the preceeding five years. However, no significant increase was observed between 1977 and 1979.

(c) La Crouzille, Vendée and Forez

Results concerning sandy sediments in a river valley at one of the sites gave values between 0.13 and 0.24 Bq/g ash, with hardly any difference between two sampling points situated 0.2 and 5.0 km downstream, respectively.

(d) Jaduguda

Measurements on bottom sediments along the Juria Nala river showed that from a mean ^{226}Ra content of 9.9 Bq/g in the zone up to 1.5 km downstream, the concentration decreased to 2.0 Bq/g at 2.5 km and to 0.78 Bq/g in the zone down to 30 km from the point where effluents are released.

(e) Witwatersrand

Radium contents in bottom sediments of rivers and lakes situated in mining areas and used for recreation or with free access to the public ranged from 0.02 to 0.26 Bq/g.

(f) Grants Mineral Belt

In this region the radium content of the tailings is almost two orders of magnitude higher than those measured in the background soils. Thus, the most prominent indicator from above-ground mineral storage in decommissioned mines is the ^{226}Ra measured in stream bed sediments. Measurements have also shown that the distance over which most tailings material settles can vary appreciably. Whereas at one site the radium concentration diminished to twice the background value in a distance of approximately 100 m at another site the distance was about 500m.

(g) Zirovski vrh

^{226}Ra has been measured in sediments (in fractions below 250 u) at 8 sampling points from the uranium mining area in 1979 to 1981 [22, 23, 24], the results ranging from 27.9 to 120.6 Bq/kg dry weight (on average around 100 Bq/kg dry weight). The results obtained were approximately one order of magnitude higher than those from background areas (the river Sava in its upper reaches - near Bohinj - around 10 Bq/kg d.w.) and approximately 10 times lower as compared to the ^{226}Ra activities (around 700 Bq/kg d.w.) of sediments in the river Sava influenced by the pollution from classic technologies (coal mines, thermal power plants).

4.4.3.3. Comments

As regards sediments in the sites investigated, it is fairly clear that practically in all cases sediments lying downstream from the point where liquid effluents are released have become contaminated.

4.4.4. Biota

4.4.4.1. Mechanisms of transfer through biota

Owing to the similarity between the chemical behaviour of radium and calcium, the former is easily metabolised by biological systems. Also, fine suspended material in water streams, particularly those which are flocculant, tend to absorb onto plant life growing in the stream. Successive uptake in the biological chain can thus lead to radium reaching man.

4.4.4.2. Specific case studies

(a) Vendée

The existence of several dams on the river produced specific environments which, having little exchange with each other, could be considered as being inhabited by homogenous ichthyological populations. Considerable differences in radium concentration levels were found to exist between the species living upstream and downstream from the release point. These differences varied between a factor 15 for the eel and 120 for the rouch. In the case of the latter, the actual concentrations were 0.37 Bq/kg fresh weight upstream and 44 Bq/kg downstream. As regards plant life, it was established that the contamination of terrestrial plants is fairly weak (1.1 to 3.7 Bq/g dry weight) in relation to aquatic plants (up to 50 Bq/g dry weight).

Cattle is often raised in the vicinity of uranium mines and mills for both milk and meat production. The mean radium content of milk over a five year period which started three years after the beginning of milling at a certain mine, were 0.078 ± 0.019 Bq/l and 0.28 ± 0.09 Bq/l at 6 km and 1.5 km, respectively, downstream from the mill. Although measurements carried out 13 years later showed no change, the levels were nevertheless high when compared with the 0.01 Bq/l prevailing in the surrounding areas. They are, however, considerably below the 1.3 Bq/l which is a derived limit for ^{226}Ra in milk.

A further experiment carried out with two sheep and one cow, which over a period of 30 days drank only mine water containing 35-55 Bq/l ^{226}Ra, showed that approximately 99% of the ingested radium was excreted in the feces. The remaining radium was divided between the urine and the milk. The mean radium content in the milk during the experiment was 0.10 to 0.17 Bq/l for the sheep and 0.19 Bq/l for the cow. After 20 days of consuming normal water again, the radium contents of the milk dropped to less than 0.01 Bq/l.

(b) Jaduguda

Extensive measurements of various biological systems in the area possibly affected by the uranium mine have been carried out. They show, for example, that the radium content of algae collected in the Juria Nala river, 2 km downstream from the release point, is about 2.1 Bq/g wet weight, with an enrichment factor of 3×10^3, while that in fish from river water containing 0.52 Bq/l ^{226}Ra could be as high as 7.9 Bq/g fresh weight of soft parts, with an enrichment factor of about 15. Algae such as Spirogyra sp. could conceivably be used as good indicators in assessing the pollution status of contaminated streams as a result of the good correlation found between the radium content of this species and that in the ambient water. The radium concentration in grass growing in soils containing between 0.01 and 4.3 Bq/g ^{226}Ra has also been measured. A reasonably good correlation between radium contents of grass and soil was found as is evident from Table 4.8. Radium concentrations in milk and vegetables measured in 1967 and again in 1972 showed an increase from 0.059 to 0.34 Bq/l in the case of milk and 0.21 to 2.3 Bq/kg in the case of vegetables.

(c) Witwatersrand

A few measurements conducted on samples of grass growing in the vicinity of decommissioned tailings impoundments gave values ranging from 0.14 to 0.32 Bq/g ^{226}Ra ashed weight. This high value is, however, attributed to visible contamination of the grassed area with tailings dust blown from the impoundments.

(d) Zirovski vrh

^{226}Ra has been measured in some selected environmental samples. Slightly increased activities of radium were found in some grasses from the area of a spent ore deposit, as well as in some plants with large leaf surfaces (Tussilago farfara and Petasites hybridus)[25]. In both types of samples the radium content ranged from 0.018 up to 0.74 Bq/g dry weight, but external contamination cannot be excluded in spite of careful sample preparation.

^{226}Ra in fish [24] (mainly trout - Salmo trutta m.fario) measured at the same time as sediments, was low at all five sampling points investigated, in general below 0.8 Bq/kg whole body fresh weight (range from 0.28 to 0.93 Bq/kg f.w.), with two exceptions from the most contaminated sites in the uranium mining area (2.5 and 2.0 Bq/kg f.w.).

^{226}Radium activities of some representative specimens of fish food [22] (Trichoptera sp. larvae and Gammarus fossarum) were on average of the same range (60 and 50 Bq/kg d.w., respectively) as in sediments from the uranium mining area.

4.4.4.3. Comments

The most important deduction which can be made in connection with radium contamination of the biota in watercourses is that relatively large enrichment by some forms of plant life, particularly algae growing in media known to be contaminated with radium, was observed.

4.4.5. Models

The quantitative description of the behaviour of radium in wastes from uranium mining and milling is essential if short as well as long-term predictions have to be made when planning the design of the waste disposal system in any uranium mining venture. This is particularly true in respect of tailings impoundments as a result of the long term implications. Several models of various degrees of complexity have been proposed recently by a number of authors [13, 14, 18] in an attempt to identify and quantify in a sufficiently precise manner the role played by the various parameters. Although a great deal of success has been achieved much has still to be done before a sufficiently generalized model is available to cope with most situations. Adding to the complexity of the problem is that fact that it does not suffice to be able to predict water movement in and out of a tailings impoundment and in the underlying soil. The chemico-physical interactions between the components of the system radium/water/tailings (and/or soil) under a variety of conditions have to be properly defined in order to make acceptable predictions regarding the behaviour of radium.

In an attempt to analyse radium migration in the earthen dam of the tailings pile at Forez after 20 years of tailings accumulation, a simple model based on the one-dimensional diffusion equation was used. The main aspect addressed was, for a certain barrier thickness, to determine the time for the concentration of radium in the water which crosses the barrier to reach a certain value. Assuming a steady-state situation and for a barrier thickness of 30 m it was arrived at a time of 19.9 years for penetration of the dam, which agrees well with the experimental data available.

4.5. RECOMMENDATIONS

(i) The effect which weathering, seepage and leaching may have on the movement of radium in the subsurface has not yet been adequately established neither is the influence of the lithographic and hydrogeologic environments on radium mobility well understood. Such information is much needed, particularly considering the effect that these phenomena may have on the long-term water quality in the water table.
The apparent immobility of radium in ground water found in some cases is cause for optimism in recommending burial of tailings. However, further experimental evidence under a variety of conditions is needed. The data can also be used as inputs in the cross-validation of mathematical models.
Having in view possible long-term effects, the behaviour of radium in and around decommissioned tailings impoundments should be examined more closely.

(ii) Pollution of surface water has been extensively documented but data on the volumes involved, which is necessary to fully describe the process, is generally lacking. Such data should be obtained.
More work should also be done on short and long-term effects of radium on agricultural ground contaminated by flood waters.

(iii) Streams sediment are the main repository of radium. Yet, the process of precipitation and redissolution of radium in field conditions is not yet fully understood. The process of redistribution and its significance to the benthic fauna and flora should be examined.

(iv) In order to make valid predictions, valid mathematical models are needed. Research on the following types of predictive models should be undertaken:

- Movement of radium in ground water
- Transport of radium in the biological cycle
- Long-term trends of potential changes that would result from an increase (or decrease) in mining activities.

It may be worth to try to identify further areas where research, development and field investigations may reasonably contribute to a better understanding of the behaviour of radium in environmental waters.

TABLE 4.1. DISSOLVED RADIUM IN GROUND WATERS IN THE JADUGUDA REGION

Description	1st year	2nd year	3rd year	4th year
1. Well adjacent to tailings pond				
^{226}Ra (Bq/ℓ)	0.017	0.017	0.017	0.018
Mn (mg/ℓ)	0.15	0.36	0.40	1.89
SO_4 (mg/ℓ)	155.7	816.4	614.4	1245.0
Cℓ (mg/ℓ)	206.9	312.5	295.3	390.0
Hardness (mg/ℓ)	885.0	1232.0	1172.0	1410.0
2. Well 500 m away from Tailings pond				
^{226}Ra (Bq/ℓ)	0.015	0.016	0.015	0.016
Mn (mg/ℓ)	0.14	0.33	0.36	0.74
SO_4 (mg/ℓ)	125.0	970.7	509.3	1158.0
Cℓ (mg/ℓ)	199.1	319.1	304.9	384.7
Hardness (mg/ℓ)	790.5	1180.5	853.6	1380.0

TABLE 4.2. RESULTS OF ANALYSES OF EFFLUENTS FROM SEDIMENTATION POND AT URANIUM MINE, NORTHERN BOHEMIA

Date of sampling	August 24 1976	Octob. 25 1976	Novem. 22 1976	Jan. 6 1977	Feb. 17 1977	March 15	May 17 1977
Water temperature (°C)	-	10.5	8	8	10	9	13
pH of the water	-	6.74	6.63	6.84	6.65	6.66	7.02
Suspended solids (mg/ℓ)	-	8	11	24	13	9	14
Total content of Ra-226 (Bq/ℓ)	10.8	1.7	9.1	5.8	2.8	3.1	5.1
Dissolved Ra (Bq/ℓ)	0.12	0.21	0.70	0.13	0.44	0.21	0.11
Suspended Ra (Bq/ℓ)	10.7	1.5	8.4	5.7	2.4	2.9	5.0
Dissolved Ra (%)	1	12	8	2	16	7	2

TABLE 4.3. RESULTS OF ANALYSES OF WATER SAMPLES TAKEN AT URANIUM MINE, NORTHERN BOHEMIA

Sampling place	Outlet of settling pond	Effluents prior to discharge into river	River just after effluent discharge	12 km downstream from discharge point
Water temperature (°C)	9.8	9.1	5.5	5.3
pH of the water	6.76±0.06	7.03±0.09	7.28±0.04	7.44±0.06
Suspended solids (mg/ℓ)	13.2 ± 2.4	18.5 ± 3.8	21.3 ± 3.7	24.0 ± 4.8
Total content of Ra-226 (Bq/ℓ)	5.5 ± 1.2	4.1 ± 0.6	1.5 ± 0.2	0.86 ± 0.11
Dissolved Ra (Bq/ℓ)	0.28±0.08	0.35±0.06	0.20±0.03	0.20±0.04
Suspended Ra (Bq/ℓ)	5.2 ± 1.3	3.8 ± 0.6	1.29±0.20	0.65±0.14
Dissolved Ra (%)	6.9 ± 2.1	8.3 ± 1.0	11.5 ± 1.3	27.2 ± 7.0

TABLE 4.4. COMPARISON OF THE RADIUM RELEASED WITH THE SOLUBLE RADIUM CONCENTRATION IN THREE FRENCH RIVERS

Mining region	^{226}Ra in effluent before BaCℓ_2 treatment (Bq/ℓ)	Receiving river	Mean flowrate ($m^3.s^{-1}$)	Conc. of soluble radium in river (Bq/ℓ)		Amount of soluble radium discharged into river (Bq/ℓ)	
				Upstream	Appr. 12 km downstream	Occurring naturally	Due to uranium mining
La Crouzille	16	Gartempe	8,19	0.040	0.10	18	37
Vendée	10	Sèvre	5,44	0.040	0.13	11	37
Forez	10	Besbre	0,25	0.078	0.31	2	18

TABLE 4.5. RADIUM CONCENTRATION IN THE EFFLUENT FROM THE PRECIPITATION POND AT TONO MINE

Unit: Bq/ℓ

	1972	1973	1974	1975	1976	1977
Jan.			0.010	0.010	0.060	0.010
Feb.			0.020	0.044	0.030	0.007
Mar.			0.044	0.030	0.010	0.007
Apr.			0.020	0.044	0.007	0.010
May			0.007	0.030	0.030	0.007
June			0.041	0.040	0.010	0.010
Jul.			0.030	0.044	0.010	0.010
Aug.			0.030	0.040	0.020	0.020
Sep.	< 0.004		0.078	0.040	0.020	
Oct.		0.030	0.080	0.030	0.020	
Nov.			0.078	0.040	0.030	
Dec.		0.030	0.167	0.020	< 0.004	

TABLE 4.6. TOTAL ^{226}Ra CONCENTRATIONS IN WATER USED FOR RECREATION OR WITH FREE ACCESS BY THE PUBLIC IN THE WITWATERSRAND REGION

Sample No	Sampling Site	^{226}Ra concentration (Bq/ℓ)
	EAST RAND:	
Vic 101/79/6W	Victoria Lake	0.007
EB 103/79/6W	Elsburg Stream	0.063
EB 104/79/6W	Elsburg Dam	0.020
EB 106/79/6W	Boksburg Lake	0.004
OR 1/79/12W	Middle Lake	0.010
OR 3/79/12W	Jan Smuts Lake	0.007
OR 4/79/12W	Geduld Dam	0.020
OR 5/79/12W	Cowles Dam	0.030
OR 6/79/12W	Vogelstruisbult Lake	0.100
OR 9/79/12W	Nigel Dam	0.110
OR 10/79/12W	Nigel Dam outlet (2 km down)	0.092
OR 11/79/12W	Withokspruit	0.007
OR 12/79/12W	Rietspruit (from Sallies)	1.630
OR 13/79/12W	Van Dyk Dam (outlet)	0.010
OR 14/79/12W	Rietspruit (Rooikraal)	0.044
	KLERKSDORP:	
SV 1/79/10W	Vaal River (downstream)	0.020
SV 2/79/10W	Vaal River (upstream)	0.010
SV 5/79/10W	Jagspruit	0.240
	ORANGE FREE STATE:	
B1/79/10W	Bosluisspruit (Beisa Mine)	0.007
B2/79/10W	Bore-hole (pt. 2) (Beisa Mine)	0.007
B3/79/10W	Bore-hole (pt. 4) (Beisa Mine)	0.020
B4/79/10W	Bore-hole (pt. 6) (Beisa Mine)	0.007
B5/79/10W	Bosluisspruit (Beisa Mine)	0.004
B6/79/10W	Sand River (pt. 1)	0.010
B7/79/10W	Sand River (pt. 2)	0.020
B8/79/10W	Sand River (pt. 4)	0.010

TABLE 4.7. BASIC DATA ON THE ANALYSED SEDIMENT AND WATER SAMPLES TAKEN ON 30TH JULY, 1979 AT URANIUM MINE IN NORTHERN BOHEMIA

Sample * No	Radium concentration	Loss of weight	"Fine" fraction	Radium content (Bq/g) in the fraction		Barium content	Radium concentration in water (Bq/ℓ)	
	(Bq/ℓ)	(% w/w)	(% w/w)	"fine"	"coarse"	(% w/w)	dissolved	particulate
4	984.70	3.4	-	-	-	50	6.22	16.74
5	180.70	13.3	95	194.50	75.96	11.2	1.22	2.41
7	12.10	6.4	28	43.59	1.89	1.5	0.11	1.48
8A	25.01	14.5	57	38.67	7.55	1.5	0.11	2.11
9	0.61	8.2	34	1.25	0.33	~ 0.05	0.03	0.16
10	0.37	4.2	28	1.12	0.17	< 0.05	0.03	0.14

* see sampling places on Fig. 4.1.

TABLE 4.8. RADIUM CONTENT OF SOIL AND GRASS AT JADUGUDA

Sample No.	Ra-226 in soil (Bq/g)	Ra-226 in grass (Bq/kg)	Transfer factor Grass x 10^{-3}
1.	0.10	2.10	21.55
2.	0.12	0.49	3.97
3.	0.18	4.18	13.6
4.	0.22	2.00	22.03
5.	0.28	4.98	17.86
6.	0.33	10.01	30.2
7.	0.49	11.57	23.75
8.	0.52	11.51	22.03
9.	0.70	9.13	13.1
10.	4.30	101.20	23.56

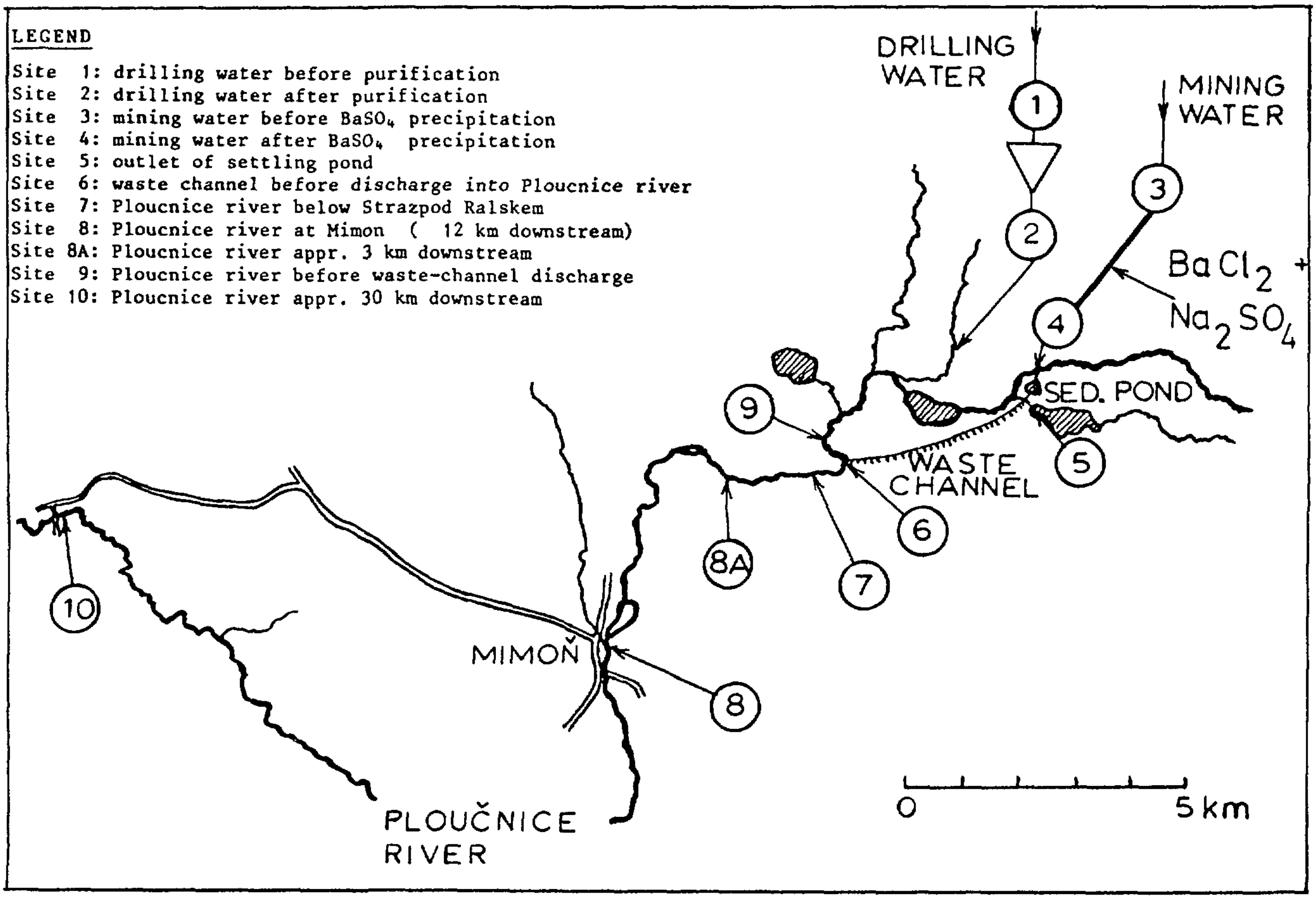

Figure 4.1. Water system analysed, with sampling places at uranium mine in Northern Bohemia.

(From Progress Report to IAEA entitled "Studies on the source, distribution, movement and deposition of radium in inland waterways and aquifers", by F. Sebesta, P. Benes, J. Sedlacek and B. Havlik. June 1980).

REFERENCES

[1] ICRP Report of Committee II on Permissible Dose for Internal Radiation (1959) - Publication 2.

[2] Management, Stabilization and Environmental Impact of Uranium Mill Tailings (Proc. NEA Seminar, Albuquerque, July 1978).

[3] Uranium Mining Waste Disposal (Proc. 1st Int. Conf., Vancouver, May 1980).

[4] STRAIN C.D., WATSON JR., J.E., FONG S.W., An evaluation of ^{226}Ra and ^{222}Rn concentrations in ground and surface water near a phosphate mining and manufacturing facility, Health Phys. 37 (1979) 779.

[5] SWIFT J.J., HARDIN J.M., CALLEY H.W., Potential radiological impact of airborne releases and direct gamma radiation to individuals living near inactive uranium mill tailings piles, U.S. Envir. Protection Agency Rep. EPA-520/1-76-001(1976).

[6] SHREVE JR. J.D., "Putting tailings in perspective radiologically, environmentally and managerially", Management, Stabilization and Environmental Impact of Uranium Mill Tailings (Proc. NEA Seminar, Albuquerque, July, 1978).

[7] STAUB W.P., TRIEGEL E.K., "Analysis of disposal of uranium mill tailings in a mined out open pit", Ibid.

[8] LAKSHMANAN V.I., ASHBROOK A.W., "Radium balance studies at the Beaverlodge mill of Eldorado Nuclear Limited", Ibid.

[9] MOFFETT D., ZAHARY G., CAMPBELL M.C., INGLES J.C., "CANMET's environmental and process research on uranium", Ibid.

[10] MOFFETT D., VIVYURKA A.J., "Control of radium-226 releases in liquid effluents", Ibid.

[11] LEVINS D.M., "Environmental impact of uranium mining and milling in Australia", Canadian Institute of Mining and Metallurgy (Proc. 9th Annual Metallurgical Meeting, Toronto, November 1979).

[12] MARTINEC M., HAVLIK B., Private communication.

[13] NELSON J.D., McWHORTER D.B., "Influence of impoundment and substractum configuration on seepage from impoundments", Uranium Mining Waste Disposal (Proc. 1st Int. Conf., Vancouver, May 1980).

[14] KLUTE A., HEERMANN D.F., Water Movement in Uranium Mill Tailings Profiles, U.S. Envir. Protection Agency Technical Note ORP/LV-78-8 (1978).

[15] KIRCHMANN R., LAFONTAINE A., CANTILLON G., BOULANGER R., Etude du cycle biologique parcouru par la radioactivité, Centre d'Etudes Nucléaires de Mol - CEN/SCK - Belgique. BLG 477 (1973).

[16] KAUFMANN R.F., EADIE G.G., RUSSELL C.R., Effects of uranium mining and milling on ground water in the Grants Mineral Belt, New Mexico, Ground Water, 14 5 (1976).

[17] EADIE G.G., KAUFMANN R.F., Radiological evaluation of the effects of uranium mining and milling operations on selected ground water supplies in the Grants Mineral Belt, New Mexico, Health Phys. 32 (1977) 231.

[18] GUREGHIAN A.B., BESKID N.J., MARMER G.J., "Predictive capabilities of a two-dimensional model in the ground water transport of radionuclides, Management, Stabilization and Environmental Impact of Uranium Mill Tailings (Proc. NEA Seminar, Albuquerque, July 1978).

[19] KAUFMANN R.F., BLISS J.D., Effects of phosphate mineralization and the phosphate industry on radium-226 in ground water in Central Florida, U.S. Envir. Protection Agency Rep. EPA/520-6-77-010 (1977).

[20] JUSTYN J., STANEK Z., Studies on the contamination of streams by naturally radioactive substances, Rep. Institute for Water Research, Prague 1968 (in Czech).

[21] RUZICKA J., Protection of waters from radioactive contamination, 7th Panel about the Problems of Radioactive Waters, CVTS, Prague 1971 (in Czech).

[22] STEGNAR P., KOBAL I.: Radioecology of uranium and radium with special reference to a uranium mining area. IAEA-TECDOC-229, Vienna, Febr. 1980.

[23] STEGNAR P., MIHAILOVIC M., KOBAL I., BRAJNIK D.: Radioecology of uranium and radium with special reference to a uranium mining area, presented at the Res. Coord. Meeting on the Radioecology of the Danube River, München, Oct. 1980.

[24] STEGNAR P., KOBAL I.: Uptake and distribution of radium and uranium in the aquatic food chain, IAEA International Symposium on Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle", Knoxville, USA, July 1981.

[25] STEGNAR P., KOSTA L., RAVNIK V., DERMELJ M., BYRNE A.R., KOBAL I.: Radioecology of uranium and radium with special reference to a uranium mining area, presented at the 2nd Res. Coord. Meeting on the Radioecology of the Danube River, Vienna, Nov. 1978.

[26] PASCHOA A.S., BAPTISTA G.B., MONTENEGRO E.C., MIRANDA A.C., SIGAUD G.M., Ra-226 Concentrations in the hydrographic basins near uranium mining and milling in Brazil, *Low-Level Radioactive Waste* Management Proceedings of Health Physics Society Midyear Topical Symposium. February 11-15, 1979. Williamsburg, Virginia, U.S.A. EPA-520/3-79-002.

Chapter 5

MIGRATION OF RADIUM IN THE TERRESTRIAL HYDROSPHERE

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5.1. INTRODUCTION

The main migration pathways of radium in terrestrial hydrosphere are outlined in Fig.5.1. Radium can enter natural waters by a number of routes including leaching of uranium ores by ground and precipitation water, discharge of waste waters containing radium in dissolved and/or suspended form, seepage from tailings ponds and leaching of radium from waste solids. Radium released by these processes contaminates ground and surface waters, where it can undergo various transformations, can be fixed on the aquifer, deposited in bottom sediments or transported to the sea. The migration of radium proceeds by a combination of natural processes which are, however, often strongly influenced by man. Transport via surface waters is susceptible to changes induced by industrial or municipal contamination of these waters and by their use for irrigation or technological purposes. The underground movement of radium can be affected by mining and exploration activities, for instance by mine dewatering, by hydraulic effects of water released from mines, by interaquifer connections via exploratory boreholes, etc.

The migration pathways depicted in Fig.5.1 represent a complex, where quite a number of possible combinations exist. In order to simplify discussion of the pathways it appears more useful to look at the individual migration media and processes separately, rather than to systematically describe the overall radium migration in specific sites. As the problems concerning radium migration can be easily grouped according to three main topics treated, the following paragraphs will discuss the processes of radium release from its sources, radium migration in ground waters and in surface waters, respectively.

It has been well established that an important role in the migration of a trace element in an aquatic system is played by the interaction of the element with solid phase in contact with the water phase. Of primary importance are also physico-chemical forms in which the element exists in water or in the solid phase. Consequently, both the physico-chemical state of radium and the interaction of radium with solid phase are given special attention in this chapter.

5.2. RELEASE OF RADIUM FROM ITS SOURCES

The various sources of radium have been briefly treated in Chapters 3 and 4. The aim of this paragraph is to discuss processes by which radium is released into the hydrosphere. For this purpose the radium sources can be divided into three groups, listed here in the sequence of their probable environmental importance as the sources of contamination of the hydrosphere with radium:

1. Radioactive waste waters and springs. Unless efficient purification methods are more widely used, waste waters from uranium mining and milling will continue to be the most important source of radium to surface waters.

2. Solids produced or modified by man, containing radium. The most important sources of this type include uranium ore stockpiles, solid wastes from uranium mining and milling, fertilizers, ash from burning fossil fuels, etc. From the point of view of radium release to the hydrosphere, these sources can be subdivided to point sources, like piles or ponds, and nonpoint sources, represented by solid particles containing radium, dissipated over large areas of earth surface.

3. Natural solids undisturbed by man, like uranium ores and other ores, subores and rocks containing radium. These sources release radium mainly to ground waters, only exceptionally, when exposed on earth surface, they are leached by precipitation and surface waters.

5.2.1. Release of Radium With Radioactive Waters

There are three main aquatic sources of radium contaminating natural waters: waste waters from uranium and phosphate milling, uranium mine drainage waters and radioactive springs. Particularly the uranium mine drainage waters have a great potential for adverse environmental impacts. The fate of radium contained in the water sources depends on the handling and treatment of the waters, schematically shown in Fig.5.2., and also on the physico-chemical forms in which radium exists in the original or treated waters.

5.2.1.1. Waste water from uranium and phosphate milling

(a) Uranium milling process

Waste water from uranium milling process represents the raffinate from solvent extraction mixed with tailings. Most of the radium contained in this mixture (slurry) is bound to tailings particles. Typical ratio of dissolved to particulate forms of radium ranges from $0.5.10^{-3}$ to 3.10^{-3} (Pradel, 1976, Levins, 1979). The slurry is usually conveyed to a tailing pond where solid particles settle out. The slurries from acid leaching process are often neutralized to pH 8-9 by lime addition. The neutralization removes most of dissolved sulfates and radium (Bakhurov et al., 1965), in the presence of tailings, however, the concentration of dissolved radium can even increase (Levins, 1979). Typical ranges of concentrations of radium and other dissolved contaminants in the waste waters derived from uranium milling process are given in Table 5.I.

(b) Physico-chemical forms of radium in such waters

Very little information exists on the physico-chemical forms in which radium exists in such waters. However, because of the high sulfate concentration remaining in the water even after its neutralization ($2-8\ g.l^{-1}$ according to Levins, 1979), a significant part of the dissolved radium must be present as neutral ion pair $RaSO_4$. From the data given in Table 5.I. the percentage abundance of the ion pair among the dissolved forms of radium can be calculated using the stability constant $K_1(RaSO_4)= 10^{2.43}$ (Benes et al., 1982). A rough calculation, neglecting the effect of ionic strength and of other equilibria in which sulfate anions participate, leads to the values of 70% for 2 g.l^{-1} SO_4^{2-} and 98% for 50 g.l^{-1}. The calculation indicates that the predominant form of radium dissolved in uranium mill waste waters can be neutral ion pair $RaSO_4$ rather than Ra^{2+} cation, which may have important consequences (see below). It should be emphasized that formation of solid phase consisting of radium sulfate only is impossible at the concentrations of radium typical for the waste waters, since neither the solubility product ($K_{so}=10^{-10.37}$, Sillén and Martell, 1964) nor the molecular solubility (as $RaSO_4$, $K_{s1}=10^{-7.94}$, Benes et al., 1982) of radium sulfate can be exceeded.

(c) Uranium tailing ponds; a possible source of contamination of ground and surface waters

Because of the high concentration of dissolved radium in uranium mill waste waters these waters should be purified before the discharge to natural watercourses. However, there remains a possibility of contamination of ground and surface waters by seepage of the unpurified water through the tailings dam. The seepage can reach as much as 10000 m^3.d^{-1} from one tailings dam (design data, Levins, 1979), but generally the seepage flow will be substantially lower. Klute and Heermann (1978) worked out a mathematical model of water movement in uranium mill tailings profiles which considers hydraulic conductivity and water retention of several fractions of tailings material (clay, silt and sand sized particles). Although the model is not designed to predict the seepage rate from a tailings pond, the data gathered and their treatment provide useful information on the seepage.

In order to prevent contamination of surface and ground waters, seepage from tailings ponds is sometimes drained or collected and then either pumped back to the pond or purified before discharging to watercourses. Even if such precautions are omitted, however, the adverse impact of the seepage is often lessened due to significant adsorption of radium on the tailings. For instance the analysis of seepage return water of a tailings pond in New Mexico revealed rather low concentration of radium (0.18 Bq.l^{-1}), contrasting with very high activity of thorium-230 and uranium in the same water (Eadie and Kaufmann, 1977). Rahn and Mabes (1978) found a few hundred times faster migration of water than of radium in tailings impoundments. Marple and Zettwoog (1980) reported that water passing through tailings dam contained about the same concentration of chlorides as the tailings pond water but its radium content was much lower. The radium retention probably depends on the material and construction of the dam. That is why in other cases the concentrations of radium in seepage were rather high (see, e.g., Kaufmann et al., 1976, who reported 1.9 Bq.l^{-1} and U.S.EPA, 1975, 2.4 Bq.l^{-1}).

Several attempts have been made to mathematically analyze radium movement in tailings dam. Zettwoog (1980) recently devised a model based on one-dimensional diffusion equation considering also the adsorption(*) of radium on particles of a watertight barrier. Using this model a good

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(*) To avoid confusion it is noteworthy that the term adsorption denotes in this chapter any process leading to concentration of radium from solution onto the surface of solids except for co-precipitation and biological uptake, i.e. it includes physical adsorption, chemisorption and electrostatic adsorption (including also ion exchange, cf. Benes and Majer, 1980).

agreement between calculated radium concentrations in seepage water and experimental data was obtained (Marple and Zettwoog, 1980). Model suitable for the solution of radium transport in lined and unlined tailings pond was described by Gureghian (1979). It is worthwhile to emphasize that when using mathematical models, the effect of the composition of seeping water on the physico-chemical form of radium and on the adsorption of radium on tailings has to be considered. Particularly the concentration of sulfates and of cations might substantially influence the migration of radium, through its effect on the formation of $RaSO_4$ ion pair and on radium adsorption, respectively. Consequently, the input data for the model cannot be based on experiments carried out in other conditions than those encountered in the specific site.

(d) Waste water from mining and milling of phosphates

Further important aquatic source of radium are waste waters from mining and milling of phosphates. Particularly waters in gypsum ponds (byproduct from phosphate milling) contain high concentrations of dissolved radium (1.8-3.7 $Bq.l^{-1}$) and can contaminate ground waters by seepage and sinkhole collapse (Kaufmann and Bliss, 1977). Such contamination, however, remains poorly documented.

5.2.1.2. Uranium mine drainage waters

(a) Origin and nature

Mine drainage waters can be subdivided into mining waters, flowing from a mine shaft/pit and directly affected by mining activities, and drilling waters from relief dewatering boreholes around the mine. The main difference between the two types of water lies in the content of suspended solids, which is very low in drilling waters and sometimes very high in mining waters. Consequently, the drilling waters contain radium mainly in dissolved forms, whereas a large percentage of radium in mining waters can exist in particulate form (see Table 5.II.). The chemical and phase compositions of drainage waters are variable and depend on the mineral being mined, its geological and hydrologic environment, mining methods and phases. Drilling waters are usually representative of ambient conditions in the ore body or in its proximity, whereas the composition of mining waters is affected by the disruptive nature of mining and by chemical or bacterial processes, mainly oxidation. The latter fact explains why, although rather stable in time, the composition of mining waters strongly depends on the mining phase and technology.

Typical variables characterizing or determining the physico-chemical state of radium in uranium mine drainage waters are shown in Table 5.II., based on the data presented by Bakhurov et al. (1965), Justyn and Stanek (1968), Hanslik and Mansfeld (1970), U.S.EPA (1975, 1979) and Sebesta et al. (1981). It is noteworthy that due to the paucity of available information the values presented are internally inconsistent and only illustrate possible variations in the parameters listed.

The particulate forms of radium in mining waters probably represent mainly radium bound to suspended particles of uranium ore or radium adsorbed on the dispersed rock. Sebesta et al. (1981) found a good correlation between the contents of the particulate radium and of suspended solids in mining waters from an underground mine. This was considered as an indication of a nearly constant content of uranium ore in the solids. Analysis by the method of selective dissolution (Benes et al., 1981) showed that about 24% of the radium contained in the same solids was soluble in 1M HCl and 21% of the radium was probably incorporated in insoluble rocks as it could not be liberated even by hot alkaline solution of ethylenediamineteraacetic acid.

(b) Purification of mine drainage waters and its effects

If significant concentrations of radium and other dangerous contaminants are present in mine drainage waters, an efficient purification should be applied before these waters are discharged to watercourses. Prior to the purification, mining waters are often conveyed to sedimentation pond to remove suspended solids which could interfere with the purification process. Concentration and physico-chemical forms of radium in purified mine drainage waters depend on the nature of waters to be purified and on the purification method employed. For instance dissolved radium has been shown to remain the predominant form of radium after ion exchange purification of drilling waters, whereas radium forms in mining waters changed towards predominance of particulate radium after purification of the waters by coprecipitation with barium sulfate and sedimentation (Sebesta et al., 1981, see also Table 5.II.). Analysis of the particulate radium in the latter case revealed that mainly barium-radium sulfate remained in the purified water, other particulate forms of radium being effectively removed by the sedimentation (Benes et al., 1980). The ratio of suspended to dissolved radium has been shown to be in linear correlation with the same ratio found for barium (Sebesta et al., 1981), indicating the validity of homogeneous distribution (Chlopin) law for coprecipitation of radium with barium sulfate (cf. Benes and Majer, 1980). It appears that concentration of barium is the main factor determining the form of particulate radium in such waters.

From the average sulfate concentration in purified and unpurified mine drainage waters, assumed equal to 100 $mg.l^{-1}$, and from the stability constant of $RaSO_4$ ion pair (see above) it can be calculated that the relative abundance of the ion pair among dissolved radium forms in such waters will be equal to or less than 10.5%. Carbonate complexes of radium can probably be entirely neglected since their stability constants are too low (Benes et al., 1982). Thus Ra^{2+} ion appears to be the predominant form of dissolved radium in mine drainage waters.

5.2.1.3. Radioactive springs

The environmental impact of radioactive springs is generally believed to be rather small, despite the sometimes large concentrations of radium in such waters (up to tens or hundreds $Bq.l^{-1}$, see for instance Belousova and Shtukkenberg, 1961, and O'Connell and Kaufmann, 1976). This is because the occurrence and water flow of highly radioactive springs are comparatively low. However, the associated pollution of the hydrosphere with radium might prove significant in the case of a large scale development of these waters for production of geothermal energy as well as for recreational and other purposes. The physico-chemical forms of radium in spring waters are very little known. Iwasaki (1969) tried to explain the mechanism of precipitation of radium contained in Japanese hot springs by coprecipitation with insoluble carbonates and ferric hydroxide.

5.2.2 Release of Radium From Solids Produced By Man

5.2.2.1. The importance of leaching processes

The processes leading to the release of radium from solids produced or modified by man can be schematically depicted as shown in Fig.5.3. Although the physico-chemical mechanism of radium release from point and nonpoint sources may be essentially the same, the different characters of these sources create different conditions for the release and thus it is worthwhile to distinguish them.

By far the greatest attention has been paid to the release of radium from uranium mine and mill tailings, as these sources represent the largest body of accumulated radium contained in solids produced by man and a potential source of the hydrosphere contamination long after the mining and milling activity that created them ceased. In some places, transport of radioactivity from uranium tailings has been identified as a major cause of radioactive pollution of surrounding watercourses (see for instance Roy and Keller, 1976, and Mansfeld and Hanslik, 1980).

Further important point sources of radium are ore and subore stockpiles, slime tailings from phosphate mining (Guimond and Windham, 1975), gypsum wastes associated with phosphoric acid plants (U.S.EPA, 1973), solid wastes from water purification processes like barium-radium sulfate (sometimes stored in lagoons - see Bryant et al., 1979) and sludges from municipal water treatment plants (Schliekelman, 1976), etc. Release of radium from the latter sources, however, has been only scarcely studied.

Very little information exists particularly on radium release from dissipated solids, as investigation of this process in nature is difficult to carry out. Furthermore, contribution of the process to the contamination of the hydrosphere with radium is often believed to be small which, however, need not be always true. For instance phosphate fertilizers can contain significant amounts of radium (about 1.6 $Bq.g^{-1}$ according to Guimond and Windham, 1975). Also the windblown dust from tailings and uranium ores can represent a substantial contribution of radium to surface runoff.

5.2.2.2. Research on leaching processes carried out in laboratory through batch experiments

Most of the research concerned with leaching of radium from various solids was carried out in laboratory. The main factors affecting the extent and kinetics of radium release were investigated, predominantly in batch experiments. These factors include the nature, composition, pretreatment and dispersity of solids, composition, volume and flow rate of the leaching solution. The first three factors largely determine the form and bond of radium in the solids and significantly influence the overall chemical composition of the leachate due to dissolution of macro-components of the solids.

(a) Effects of the nature of solids

The effect of the nature of solids was demonstrated by Iyengar et al. (1979) who found that river water and distilled water leached virtually no radium from monazite ore, whereas leachability of uranium ore ranged from 0.005% to 0.018% of the radium contained in the sample and that of uranium ore tailings was about ten times higher. Solutions of 1M ammonium acetate and 0.05M hydrochloric acid leached more than one order of magnitude higher amount of radium from uranium ore tailings than from lignite fly ash. The higher leachability of uranium ore tailings was explained by a labile state of radium in ore attacked by milling and by chemicals. Havlik et al. (1968) also found higher leachability of uranium mill tailings than of uranium ore.

(b) Effects of the leaching conditions

Most of the leaching experiments were carried out with uranium mill tailings from the acid leach process. It has been found that kinetics of radium liberation from the tailings is very rapid, maximum liberation being achieved after 90 s - 30 min if the suspension is well stirred (Shearer and Lee, 1964, Havlik et al., 1968, Levins et al., 1978, Levins, 1979). With the exception of the first quoted paper, the authors observed decrease in the concentration of liberated radium after the maximum. Ryan and Levins (1979) interpreted the rapid initial dissolution of radium as being controlled by mass transfer either from the surface of the particles or from readily accessible pores. The subsequent decrease was explained by the increase of sulfate concentration in solution due to dissolution of sulfates from tailings, which induced reprecipitation of radium. These findings suggest that a significant part of radium rests on the surface of tailings particles. No direct data on the chemical form of the surface radium is available but it can be assumed that the radium is coprecipitated with barium or calcium sulfate.

The primary factor affecting the percentage of radium leached from tailings has proved to be the ratio of the volume (V) of the leaching solution to the weight (m) of the leached sample, V/m or liquid/solid ratio. According to Levins et al. (1978) the almost linear increase with V/m of the percentage of radium leached by demineralized water, observed by them (see Fig.5.4.), is analogous to dissolution of sparingly soluble salt. Shearer and Lee (1964) found a more complicated effect of V/m. The amount of radium leached with distilled water did not increase until a certain threshold value of V/m was reached. The increase above this value was rather steep but it slowed down reaching eventually a maximum leached amount. The effect of liquid/solid ratio was greater for acid leach mill tailings than for tailings from alkaline leach process, probably due to different quantitites of sulfates associated with the two sorts of tailings. The percentage of radium leached at a given V/m ratio was reported by the authors to depend on the quantity of solids (or the total radium reservoir), which is difficult to explain.

Several authors studied repetitive leaching of one sample of tailings with fresh portions of leaching solution (Misawa et al., 1964, Shearer and Lee, 1964, Levins et al., 1978, Ryan and Levins, 1979). From the results reported it can be concluded that the amount of radium leached with consecutive portions of the solution generally decreases and the character of the decrease depends on the leached sample, composition of the leaching solution and the liquid/solid ratio. For instance Shearer and Lee (1964) and Levins et al. (1978) observed the largest drop in the concentration of radium in leachate in the first leaching stages, whereas Misawa et al. (1964) found such drop only after eight leaching stages.

The latter authors explained the drop as being due to complete removal of calcium sulfate containing the easily soluble part of radium. The close interrelation of cummulative amount of radium leached and of the V/m ratio is demonstrated in Fig.5.5.

(c) Effects of the nature of the leaching solutions

Most of the leaching experiments were carried out with water, either pure (distilled, demineralized) or natural. It is certain, however, that the composition and pH of the water changes in contact with the tailings due to dissolution of tailings soluble components. In order to check the possible effects of such changes as well as the effects of variable composition of natural or waste waters, experiments were undertaken with leaching solutions of variable composition and pH. Analysis of the pH-effect carried out by Havlik et al. (1968) and Iyengar et al. (1979) has led to the conclusion that radium liberation from tailings only moderately depends on pH in the pH region 2-13, whereas a substantial increase in the liberation was observed at pH 1-1.6. On the other hand, Levins et al. (1978) described a more pronounced pH-effect, depending also on the liquid/solid ratio and concentration of sulfates (see Fig.5.6.). The difference between the two findings may be due to different type of tailings studied as well as to different V/m ratio.

Havlik et al. (1968) studied the effect of several cations at 0.01, 0.1 and 1M concentrations on the leachability of radium from tailings. They found that almost all radium present in tailings can be liberated by 1M solutions of potassium and sodium chlorides. The leaching ability decreased in the order KCl> NaCl> $CaCl_2$> $MgCl_2$, the addition of barium chloride to water actually diminished the release of radium. The authors explained their results by the assumption that radium is bound in tailings by adsorption on clay minerals. However, besides of the competitive effect of added cations in such adsorption the results might also be explained by the effect of added salts on the solubility of barium sulfate, carrying radium. The latter explanation is supported by some data published by Ryan and Levins (1979), indicating increased release of barium from tailings due to addition of sodium chloride while release of calcium and strontium remained almost unchanged after the addition.

Levins et al. (1978) and Ryan and Levins (1979) investigated the effect of certain salts in more detail. They clearly demonstrated that increased concentration of sulfates in leaching solution strongly suppresses radium release from tailings (see Fig.5.7.). This correlates well with another finding by the same authors that a larger content of sulfates in tailings is connected with lower leachability of radium. The linear dependence of the percentage of radium leached on the concentration of sulfates (Fig.5.7.) can serve as further argument in favour of the release of radium via the mechanism of barium sulfate dissolution. Negative effect of sulfates on radium leachability was found also by Shearer and Lee (1964) who reported that more radium was released from tailings contacted with distilled water than from the same tailings contacted with river water, containing sulfates.

(d) Effects of the composition of tailings

Very few concrete data can be found on the effects of tailings composition and pretreatment on radium leachability, although previous discussion has indicated at least some qualitative differences among various tailings. Ryan and Levins (1979) found difference among different samples of tailings in the percentage of radium that cannot be extracted from the tailings even after prolonged, multistage treatment with 3-5M NaCl. These effects merit further study, in which particularly the bond of radium in tailings should be quantitatively characterized. Method of selective dissolution (Benes et al., 1981) can be used for this purpose.

(e) Effects of natural processes and biota

Leachability of tailings might be significantly influenced also by natural processes, for instance by bacterial oxidation or ageing of tailings. The bacteria (for instance Thiobacillus ferrooxidans) are assumed to promote the oxidation of ferrous ion to the ferric state, leading in the presence of pyrite to the formation of sulfuric acid. In order for T.ferrooxidans to function in biological oxidation of sulfides, the pH must be below 4 (preferably in the range from 1.5 to 3) and oxygen must be available. The biological leaching is also affected by the temperature, the rate of leaching decreasing as the temperature decreases (below 35°C).

Bacterial activity has been noticed as deep as three metres in tailings piles (Mrost and Lloyd, 1971). Some laboratory experiments to assess the effect of bacterial oxidation on radium release from tailings are currently being conducted in South Africa (De Jesus et al., 1980). The ageing effect has been observed by Levins et al. (1978), who have also shown that the dispersity of tailings particles and temperature have only a small influence on the percentage of radium leached.

The laboratory experiments have proved that significant amounts of radium could enter water phase if uranium tailings were discharged into a river. Although the rate of the release would be probably low due to the sulfate content of natural water and the leached amount would decrease with time, the tailings particles deposited on river bed and scoured during high water flows would represent a long lasting source of radium to the water environment. Therefore it is imperative to prevent both intended and inadvertent discharge of uranium tailings to watercourses.

5.2.2.3. Research on leaching processes carried out in laboratory through simulated pile conditions

Several model experiments were undertaken to study the leaching in simulated pile conditions. These experiments consisted of packing the material to be leached in column. The content of radium in the effluent from the column was measured as a function of the time or the volume of water passed and as a function of composition of solids or leachate.

A rather extensive study of this type was done by Bryant et al. (1979), who investigated leaching of radium with water (the flow rate equivalent to 41, 82 or 460 mm precipitation per month) from abandoned uranium mine tailings, lime treated abandoned tailings, abandoned tailings with top layer of Ba(Ra)SO_4 sediment, fresh tailings, chemically fixed fresh tailings, mixture of sewage sludges and revegetated tailings and mixture of chemically fixed and sludged revegatated tailings. The composition of the abandoned tailings was quartz, pyrite, calcium sulfate (from neutralization by lime at discharge), metal hydroxides etc., the pH value of seepage or runoff water from these tailings ranged from 1 to 3. The fresh tailings were characterized by a substantially higher pH of water in contact with them: the pH of leachate from untreated tailings was about 7.5, the chemically fixed tailings stabilized it at about 12. The leaching experiments were supplemented with the study of radium release from untreated or chemically fixed sediments of $Ba(Ra)SO_4$ in a simulated settling pond. The sediments came from the purification of seepage and runoff waters from abandoned mine tailings carried out by the addition of lime (to pH 9) and barium chloride. No details of the chemical fixation are given but the fixation was probably done by the method proposed by Rubinsky (1975). The authors arrived at the following findings and conclusions:

1) Leaching of radium from abandoned (treated or untreated) tailings was approximately constant for the first 12 months, radium-226 activity ranging from 0.7 to 3.7 $Bq.l^{-1}$. During the next five months the activity of radium in leachate increased to 3.7-6.5 $Bq.l^{-1}$. The water flow rate (41 or 82 mm) exerted little influence on the leachability of radium in the first 12 months, whereas the higher water rate leached more radium in the next five months. However, the highest water flow rate led eventually to the same activities of radium in leachate as those found with the lowest rate (see Table 5.III.). Addition of lime to the top of column had no apparent effect on the leachability of radium. On the other hand, the top layer of $Ba(Ra)SO_4$ sediment increased radium activity in the leachate by about 30% or more except at the highest flow rate. Consequently, lime applied to the surface of abandoned tailings sites at rates recommended to support revegetation should have no effect on the radium leaching, whereas recycling $Ba(Ra)SO_4$ sediments resulting from the treatment of seepage and runoff from abandoned mine tailings back to the surface of these sites is not an acceptable disposal method.

2) Leachability of radium-226 from the chemically fixed fresh tailings was considerably lower than from the non-fixed tailings. The application of sludge to the fresh tailings (both fixed and non-fixxed) resulted in an increased activity of radium in leachate, probably due to degradation of the organics in the sludge(Table 5.IV.).

3) Leachability of radium-226 from the sediment $Ba(Ra)SO_4$ was rather low: activities in the leachate did not exceed 0.33 $Bq.l^{-1}$ ^{226}Ra. Chemical fixation of the sediment resulted in substantial decrease of the leachability.

Levins et al. (1978) found, in similar experiments with uranium mill tailings leached with demineralized water, that radium concentration in leachate decreased initially but after a few months approached a constant value of 0.9-11 $Bq.l^{-1}$. This concentration was approximately the same as that measured in aged, neutralized tailings slurries. The volume of water that passed through the column was the most significant factor affecting the amount of radium leached.

Kurokawa and Kurosawa (1980a) compared leachability, by rain water, of untreated uranium ore and of the same ore preliminary leached with sulfuric acid. About one ton of the ore was placed in cylinder 0.6-1 m in diameter and exposed to natural precipitation. Rain water passing through the ore column was collected and analyzed monthly for radium. It has been found that relative solubility of radium, expressed as $Bq.l^{-1}$ per μg of radium in the ore, amounted to $1.5.10^{-2}$ in the first 600 l of rain water passing through the treated ore, whereas it was about $1.1.10^{-4}$ after more than 2000 l of rain water passed through the untreated ore. The easier elution of radium from the treated ore was explained by the porous structure after the treatment and by the sulfuric acid remaining in the ore, which decreased pH value of the passing water from 7.5-8.7 to 2.7-3.7. The difference found, however, might also be at least partially ascribed to the different volumes of water passed through the treated and untreated ores.

Movement of rain water in tailings piles was mathematically modelled by Klute and Heermann (1978). The authors came to the conclusion that under limited rainfall conditions, any significant vegetative cover on the tailings pile would use all the available precipitation, leaving little or no water to flow to greater depths in the pile. They also concluded that rainfall could penetrate to the watertable even in arid climates.

5.2.2.4. In situ studies

Data on actual release processes from solids occurring in nature are scarce. They are mostly confined to random observations in the vicinity of uranium mines or mills, indicating local surface water contamination immediately downstream from tailings or spoils piles (see for instance Mansfeld and Hanslik, 1980, Shinpaugh et al., 1980b). An indication of radium release from point solid sources need not be sought only by the analysis of waters related to the source. Because of the ability of soil to bind radium (see 5.3.), the data on radium content in soil underlying the source or close to it can also be used for this purpose. For instance Shinpaugh et al. (1980ab) detected in this way spread of radium around an inactive uranium mill site. Similar findings were made elsewhere (U.S.EPA, 1979). De Jesus et al. (1980), on the other hand, analyzed the underlying soil of a 40 years old tailings impoundment and concluded that the contamination of the soil by radium from the tailings was very low, indicating a low mobility of radium in the tailings.

Analyses of soil and water samples in the neighborhood of tailings piles revealed that tailings particles are sometimes transported by water (Shinpaugh et al., 1980a, U.S.EPA, 1979, Kribek et al., 1979). The particle transport depends on erosion of the pile and therefore can be greatly reduced by revegetation or other stabilization of the pile (U.S.EPA, 1979).

5.2.3. Leaching of Radium in Ground Waters

5.2.3.1. Natural processes leading to the release

Processes leading to the release of radium from rocks to ground waters are sometimes denoted as "primary" migration, in contrast to "secondary" migration of the released radium in ground waters, mine drainage waters and surface waters. From the general knowledge of the factors affecting dissolution of minerals in ground waters (see, e.g., Posokhov, 1969, and Garrels, 1976), it can be deduced that transition of radium from a rock to ground water will be determined by the type of the rock (due to variable solubility of rocks or variable physico-chemical state of radium in rocks), by composition of ground water, characteristics of the water movement, temperature and time interval of contact of the water with the rock. The release can be studied either by model experiments or by correlating radium contents found in groundwater samples. Because of the very complex character of natural processes leading to the release, the analysis of the effect of individual factors on the release can be more easily done by model experiments and therefore most of the information discussed here was obtained in the laboratory.

5.2.3.2. Influence of the nature and of the texture of the rocks (laboratory studies)

Some results of experiments with uranium and thorium ores have already been mentioned in the previous paragraph (5.2.2.). Starik and coworkers (Starik, 1959, Starik and Lazarev, 1959) found that leachability of radium from different minerals considerably differs. The same conclusion can be drawn if the results obtained by different authors are compared: for instance Starik's data with those published by Havlik et al. (1968) and Iyengar et al. (1979). In the comparison, it is necessary to take into account possible effect of the liquid/solid ratio, discussed in 5.2.2.

Zaborenko et al. (1959) and Starik and Lazarev (1960) observed a pronounced effect of particle size of monazite on the leachability of radium. The percentage of radium leached for instance with 0.2M hydrochloric acid (without a significant dissolution of the ore) increased from 0.39% for 3-5 mm particle size to 3.0% for less than 0.07 mm. The effect was explained as due to the greater surface area of crushed ore and to a change in adsorption properties of the surface, and without doubt represents one of main reasons why the release of radium from rocks is enhanced by weathering process.

5.2.3.2. Influence of the leaching solution composition (laboratory studies)

Considerable discrepancy exists among the results of various authors as to the effect of leaching solution composition. Several authors reported an enhanced release of radium due to increasing concentration of salts in leaching solution, but the order of cations obtained by comparing their leaching effect was very different. Starik (1959) reported the order

$$H^+ > Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > K^+ \gg Na^+$$

for unspecified minerals, whereas data by Havlik et al. (1968) correspond to the order (Table 5.V.):

$$K^+ > Na^+ > Li^+ \sim Ca^{2+} \sim Mg^{2+} > Sr^{2+} \sim Ba^{2+}.$$

All the authors explained the effect by the desorption action of the cations added. Lazarev (1959) found that leachability of radium from monazite increased with the concentration of salts only to a certain limit, which depended on the acidity of the solution and was different for ^{224}Ra and ^{226}Ra (see Table 5.VI.). The difference between the two isotopes was probably due to their different bond in the mineral. Acidity of water was also reported to affect solubility of radium from minerals. Starik (1959) found a pronounced increase in radium leachability from monazite at pH lower than 4, Havlik et al. (1968) observed only moderate effect with uraninite (Table 5.V.).

Study of the kinetics of radium release has revealed (Havlik et al., 1968) that the release in laboratory conditions is a rapid process, maximum amount of radium being leached after about 30 min. contact. The authors described a decrease in radium concentration after the maximum. The time course of concentration of a species dissolved in solution passing through a maximum is quite common in leaching and dissolution of minerals and soils, particularly at low liquid/solid ratios (Lerman, 1979). It indicates simultaneous occurrence of dissolution and adsorption or precipitation. Lerman (1979) presented a general theory of this phenomenon.

Starik's (1959) results pointed to an important role of diffusion in the leaching process. The leached amount rapidly decreased in a series of consecutive leachings with fresh portions of solution, but it reached the original value after the leached sample was left to recover for 1.5 year. The latter effect and other results led Starik (1959) to the conclusion that mechanism of radium release from minerals (rocks) without dissolution of the minerals is characterized by three stages:

1) Radium migrates from crystal lattice of the mineral, where it is formed in an interstitial position (except for ^{228}Ra), to thin capillaries or pores in the mineral. The migration is due to recoil energy of the formation or due to diffusion.

2) Adsorption equilibrium is established between radium in the capillary water of the mineral and radium on the capillary wall, whereby most of radium is adsorbed on the wall.

3) During the contact of the mineral with ground water, radium contained in the capillary water diffuses out of the capillaries (if suitable concentration gradient exists) and can be desorbed from the capillary walls.

The combined effect of the recoil and diffusion explains differences found between relative leachability of genetically bound isotopes of radium from the same rock specimen (monazite, uraninite, see Starik, 1959, and Zaborenko et al., 1959).

5.2.3.3. In situ studies

When extending the conclusions drawn from laboratory experiments to ground waters it must be kept in mind that the rate and magnitude of in situ leaching will be probably lower than those found in laboratory experiments, as the partial degradation of rocks during their mining or laboratory grinding, oxidation of the rocks in contact with the atmosphere and their possible bacterial attack in laboratory experiments can substantially increase leachability of the rocks. However, some of the conclusions were corroborated by analyses of ground waters. For instance Kaufmann and Bliss (1977) found that radium-226 levels in ground waters from Sarasota Country in Florida increase with salinity of the waters, in accordance with the results of laboratory experiments mentioned above. Tanner's (1964) results indicated an increased concentration of radium in ground waters enriched in chlorides, pointing to the role of chloride anion in dissolution of radium from rocks. Kanroji et al.(1979) came to the conclusion that increased concentration of calcium in thermal springs of Shirahama spa can be the principal factor of occurrence of radium in the spring water.

According to Tokarev and Scherbakov (1956), concentration of radium in natural waters is determined by a complex of physico-geographic, geologic, hydrogeologic, physico-chemical, physical and biological factors. In a rough analysis of available data on radium content in natural waters, the authors distinguished ground waters from sedimentary rocks, siliceous igneous rocks and uranium deposits. The second important parameter considered was whether the corresponding aquifer system was stagnant or circulating. The highest value of mean radium concentration was reported for stagnant ground waters from sedimentary rocks (~ 11 Bq.l^{-1} ^{226}Ra), whereas stagnant waters from siliceous igneous rocks were found to contain an average 0.15 Bq.l^{-1} ^{226}Ra and circulating waters from both the types of rocks contained only 0.07 Bq.l^{-1}. The average content of radium-226 presented for waters from uranium deposits was 2.2-3.0 Bq.l^{-1}. Further data but without an extensive analysis can be found in Scott and Barker (1962), White et al.(1963), Mansfeld and Zajicek (1969) and Kaufmann and Bliss (1977).

Apart from the uranium ores and other rocks untouched by man the groundwater leaching of radium can also take place in underground or open pit mines and in abandoned mines backfilled with tailings. Impact of such leaching on ground water quality can be enhanced by the higher leachability of disrupted, oxidized ore in mine as well as of the tailings than of the undisturbed ore (cf. above). These processes, although likely, remain little documented. Similarly, the ground water quality impacts of in situ (solution) mining are poorly known. Some indication of the occurrence of such processes can be found from data on radium concentration in waters from abandoned mines and in water from wells adjacent to mines. For instance Wukasch and Cook (1972) found a large radium activity in a well situated close to an active uranium mine and in water from inactive mines filled with ground water. In contrast, water in an exploratory well drilled into an unmined ore body contained ten times less radium.

5.3. MIGRATION OF RADIUM IN GROUND WATERS

Our knowledge of radium migration in ground waters is not satisfactory. Of the relatively few data published on this problem, most were obtained by analyzing water samples from wells in proximity of surface point sources of radium. The information gained in this way is related mainly to the infiltration process, some conclusions can be drawn, however, also on the lateral migration.

5.3.1. Information Gained on the Infiltration Process

5.3.1.1. Removal of radium during infiltration

The infiltration of radium containing water through soil, subsoil and rocks represents probably the most important kind of groundwater migration from the point of view of contamination of ground waters with radium caused by man. The information gathered as yet seems to indicate that such contamination has been relatively low, particularly when compared to the contamination of ground waters with other contaminants from the same sources. For instance Kamath et al. (1972) and Iyengar et al. (1979) found very little increase of radium activity in wells adjacent to uranium mill tailings pond during 3-4 years, while concentration of uranium, sulfates, chlorides and water hardness increased very significantly (see Table 5.VII.). An extensive study of the impact of uranium mining and milling on ground waters was undertaken by U.S. Environmental Protection Agency in New Mexico, where a large seepage from tailings ponds occurred (U.S.EPA, 1975, 1979). Despite the seepage, little contamination of shallow aquifers was found. Similarly, data on radium concentration in ground waters indicated that extensive phosphate mining and milling in Florida probably did not appreciably change radium-226 levels in Florida ground waters (Kaufmann and Bliss, 1977).

The low contamination cannot be explained only by the dilution of infiltrating waste waters with ground waters and therefore points to an efficient mechanism of radium removal from the infiltrating water. This mechanism is generally believed to be the high adsorption of radium on soil, subsoil and rocks (see, e.g., Justyn and Stanek, 1968, and U.S.EPA, 1979).

5.3.1.2. Laboratory experiments on radium adsorption by soil

Laboratory experiments on radium adsorption by soil were undertaken by Kirchmann et al. (1973) who determined distribution constant (K_D) of radium between solution and two types of soil and found that radium adsorbs more on peat (K_D = 1500-2500 $cm^3.g^{-1}$) than on sand (K_D = 150-200 $cm^3.g^{-1}$).

Strong binding of radium in soil has been documented by leaching experiments with soil samples containing high amounts of radium, either natural (Shuktomova et al., 1978), or from uranium refinery waste disposal (Phillips and Nathwaniyi, 1978). In the first case, three kinds of radium bond were distinguished in turf-meadow and gley-highly podzolic soils. The authors came to the conclusion that proportions of these bonds vary in depth and depend on the physico-chemical properties of the genetic horizons, but most of the radium in soil is well fixed. This conclusion well corresponds with findings by the latter authors that leaching of radium from soils under simulated natural conditions is rather slow and diffusion-controlled.

5.3.1.3. Field data and modelling on vertical transfer

Kribek et al. (1979) studied vertical distribution of radium in soil profiles in an area of uranium mining. They found that the distribution depends on the type of soil profile. In the case of floodplain soil significantly contaminated by radium due to periodical flooding with river water receiving mine effluents, about 79% of the radium contained in the top 60 cm of the soil was cumulated in the surficial layer (0-10 cm) and 18% was in the 10-25 cm layer. Latter finding seems to substantiate results obtained by Justyn and Stanek (1968) who calculated the movement rate of radium during seepage of water through a soil layer using relations suggested by Boenzi et al. (1965) and Dlouhy (1967). Applying the value of 2000-3000 $cm^3.g^{-1}$ for the distribution constant K_D and 3-5 $g.cm^{-3}$ for ratio of mass to pore volume of the soil, they arrived at the rate of radium movement equal to or less than 10^{-7}-10^{-8} cm.s^{-1}. The authors stated that the migration rate could be further slowed down by soil clogging and swelling. The calculation related to the case of seepage of neutral water and did not consider the effect of acidity which could enhance mobility of radium in soil (see Phillips and Nathwani, 1978). However, the retardation of the migration in ground waters of radium released with acid wastes would be aided by rapid neutralization of the wastes in soil layer or by mixing with ground waters (Kaufmann and Bliss, 1977).

A mathematical model of radium migration considering the adsorption and neutralization effects during seepage of acid wastes through a nonhomogeneous aquifer has been suggested by Gureghian (1979). The author calculated isopleths for several relative concentrations of radium (C/C_o = 0.005, 0.05 and 0.8 where C/C_o is the ratio of radium concentration at a given site to its original concentration at the beginning of migration) and for the migration periods of 5, 20 and 30 years. Analysis of the results has shown that the rate of migration of radium from surface acid wastes can be quite appreciable for the initial period of 5 years after which it decreases. The calculated migration path for C/C_o = 0.005 and 20 years does not exceed several hundred meters. Rather low K_D values were assumed ($\leq$100 cm^3.g^{-1}). Similar calculation quoted by U.S.EPA (1979) resulted in much smaller movement of radium in ground water beneath and adjacent to a uranium mill tailings pond: several meters after 20 years.

The conclusions drawn above for seeping waste waters can be extended for the infiltration of dissolved radium coming from other, nonpoint sources like irrigation, fertilizers, radium containing dust etc., since the migration mechanism is the same. Because particulate radium is also retained in soil due to filtration effect, the soil layer appears to be an efficient barrier preventing or reducing contamination of ground waters from all kinds of surface radium sources. Where the soil layer is lacking, the route of radium from surface sources to ground waters is probably easier. Although this is poorly documented, the easiest route of radium to shallow ground waters should be infiltration through bare stream beds, whereas seepage from settling ponds does not seem to represent so easy route because of the self-sealing effect of fine sediments (U.S.EPA, 1979).

5.3.2. Information on Migration of Radium in Aquifers

5.3.2.1. Field data on longitudinal migration

Information on the lateral migration of radium can be derived from data related to locations where seepage from surface point sources evidently contaminated the underlying or adjacent ground waters. Radium content in samples of well water is to be evaluated as a function of distance from the surface source and of the direction. However, a reliable analysis of radium migration from such data can be made only if sufficient information on movement of ground water and on the properties of aquifer is available and if the "background" activity of radium in the given area is low and sufficiently stable. Generally such an analysis is impeded by the fact that a high radium content in ground water can also be a natural phenomenon and not necessarily indicative of the migration from the surface source (Kaufmann and Bliss, 1977). Natural radium concentrations from 0.0037 to 370 $Bq.l^{-1}$ were reported for ground waters (Tokarev and Shcherbakov, 1956).

Several cases of local contamination of ground waters with radium from surface sources have been described in the literature (Bakhurov et al., 1965, Justyn and Stanek, 1968, Kaufmann et al., 1976). In all the cases, the extent of contamination rapidly decreased with distance from the source, indicating rapid immobilization of radium, probably due to adsorption on soil. A strong interaction of radium with rock follows also from the experience gained from injection of radium containing waters into deep wells. Lynn and Arlin (1962) found that 0.028 m^3 of rock is capable of adsorbing about 10^{-7}g of radium by ion exchange.

To the author's knowledge, no distant groundwater migration of radium from surface sources has been described. However, the occurrence of radioactive waters sometimes found in a large distance from their probable natural source might indicate a long range migration of radium. Determining role in this respect belongs mainly to the hydrogeologic conditions in the aquifer, such an occurrence being more probable in aquifers with a large water circulation, for instance in sedimentary rock aquifers (Mansfeld and Zajicek, 1969). The migration of radium will also depend on the physico-chemical form of radium and on the composition of ground waters. Salinity of some types of ground water which is known to enhance radium solubility from rocks (cf. 5.2.3.) probably promotes the mobility of radium due to suppressing its adsorption on aquifer.

5.3.2.2. Interaquifer migration

Interaquifer migration of radium is very poorly known. From the data published so far it can be concluded that the natural infiltration of surface waters contaminates only shallow aquifers. It is improbable that radium thus added will reach deep bedrock aquifers (U.S.EPA, 1979). An example of the interaquifer migration of radium imposed by man can be found in the data presented by Kaufmann et al. (1976). Monitoring the chloride and uranium concentrations in the vicinity of an injection well where waste waters containing large amounts of contaminants including radium were injected, the authors detected leakage from the injection zone, situated more than 100 m beneath the monitoring well. The concentration of radium in the monitoring well was 10 times higher than the average background in that area, indicating upward movement of radium. The interaquifer movement of contaminants casts doubts on the suitability of the injection as a disposal method for radioactive wastes (Kaufmann et al., 1976).

5.3.3. Physico-chemical Form of Radium in Groundwaters

Almost no data exist on the physico-chemical form of radium in ground waters. It is very likely that the particulate or colloidal forms of radium will be rare in undisturbed ground waters due to the filtration effect and due to the large surface area of aquifer available for surface adsorption and precipitation processes. A large underground reservoir with a small solid surface to water volume ratio may be an exception as far as colloidal forms are considered. Water samples taken from wells or from springs need not represent the actual state in ground waters since they can be affected by contact with atmosphere and by dispersion of solid particles during sampling. Eadie and Kaufmann (1977) determined the average abundance of particulate forms of radium in water taken from three wells to be 24%. The data given for drilling waters in Table 5.II. were much lower. Among the soluble forms of radium the $RaSO_4$ ion pair can again prove important as sulfate concentrations in ground waters may be rather high (values as high as 9.23 $g.l^{-1}$ were reported by White et al., 1963). Because of the extremely high content of HCO_3^- ion in some waters (up to 15.2 $g.l^{-1}$ according to White et al., 1963), neither the formation of hydrogencarbonate and carbonate complexes of radium can be ruled out.

5.4. MIGRATION OF RADIUM IN SURFACE WATERS

Quite an amount of data has been published on the concentration of radium in surface waters, both unaffected by man and contaminated with radium due to uranium mining and milling or due to other human activities (see Chapters 3 and 4). Much less information exists on principal laws determining radium migration in surface waters and very little attention has been paid to the physico-chemical state of radium in surface waters, althouth the state and its changes form a necessary basis for better understanding the migration.

Natural concentrations of radium in surface waters tend to be rather low, varying between 0.001 and 0.3 $Bq.l^{-1}$ for ^{226}Ra (Tokarev and Shcherbakov, 1956, Belousova and Shtukkenberg, 1961, Miyake et al., 1964). Discharge or seepage of radium containing waters and runoff from radium-contaminated areas can add to surface waters significant amounts of radium, whose further fate is determined by many factors. In order to facilitate discussion of the effects of these factors, migration of radium in surface waters can be subdivided into several stages schematically depicted in Fig.5.8. (As virtually no data are available on the migration of radium in runoff water from radium-contaminated areas, this type of migration has not been included in the scheme). The discussion will follow the sequence of the framed processes. Due to the importance of sediments for radium migration in surface waters, the radium interaction with sediments will be discussed in detail separately (see 5.5.).

5.4.1. Migration in Wastewater Channel

Experience shows that wastewater channel need not be only a stream conducting waste water to natural recipient but also a site where significant changes in concentration and/or forms of radium can take place. Many waste waters represent disequilibrium systems where rapid chemical reactions occur. For instance mine drainage waters often contain ferrous ions which are oxidized in contact with air. The ferric iron formed in this way hydrolyzes and gives rise to flocs of ferric hydroxide coprecipitating part of radium present in waste water in dissolved form (Benes et al., 1978). Analysis of waste water purified by precipitation of barium sulfate and flowing from a settlement pond revealed that the precipitation of barium sulfate can continue in wastewater channel, resulting in significant changes in the abundance of suspended forms of radium with time (Sebesta et al., 1980).

Several authors noticed a decrease in radium concentration along the wastewater flow. U.S.Environmental Protection Agency conducted study of radium movement in mine drainage water in an arid area of New Mexico where uranium mine dewatering or mill discharge caused the only flow in a dry river channel. Dissolved radium was found to rapidly decrease with distance (e.g. from 1.1 $Bq.l^{-1}$ to 0.03 $Bq.l^{-1}$ in 9.2 km), probably due to strong adsorption onto the stream sediments (U.S.EPA, 1975, 1979). An analysis of migration of radium released with tailings pond water during an accident in New Mexico also led to the conclusion that radium was rapidly removed from the waste water by sorption or precipitation (U.S.EPA, 1979).

The radium removal in wastewater channel can strongly depend on the character of the channel. For instance Sebesta et al. (1978) noted a significant change in sedimentation of radium in a wastewater channel due to regulation of the channel. After the regulation most of the sediments which originally settled down in the channel were transported into receiving river.

5.4.2. Mixing With Receiving Natural Waters; the Deviations From the Mixing Law and the Role of Solid-liquid Interactions

The process of mixing (waste) waters containing dissolved and particulate radium with natural receiving waters is connected with two important effects on the concentration and forms of the radium: effect of dilution and of change in water composition. Dilution has been shown to be the principal factor leading to decrease of radium concentration in river systems (see for instance Iyengar et al., 1978, Kobal et al., 1978, U.S.EPA, 1979, Sebesta et al., 1981). The effect of dilution with stream water can be generally expressed by the formula (mixing law)

$$c_x = \frac{c_w \cdot Q_w + c_s \cdot Q_s}{Q_w + Q_s}$$

where c_x is the concentration of radium (total or of some of its forms) after the dilution and c_w, c_s, Q_w, Q_s are the corresponding concentrations of radium in waste water (w) and in stream water (s) before the mixing and the corresponding flow rates, respectively. Validity of this formula for dilution of radium containing waters was examined by several authors. Justyn and Stanek (1968) analyzed the effect of dilution of uranium mine effluents with river water on the concentration of radium downstream from the effluent discharge at several localities in Czechoslovakia and claim that the c_x value calculated using the above formula has to be multiplied by a correction factor ranging from 1.2 to 2.5 in order to get the correct (measured) radium concentration. The authors did not discuss why the mixing law was not valid in the studied cases. Sebesta et al. (1981) found a good coincidence between the calculated and measured values of c_x for dissolved, particulate and total radium at the confluence of uranium mine waste waters purified by precipitation of barium sulfate and of a small river (see Table 5.VIII.). The coincidence indicated that other factors than the dilution were unimportant there or their effects were counterbalanced. Such processes as adsorption of radium on river water suspended solids or stabilization of the concentration of dissolved radium by dissolution of its particulate forms were probably too slow to significantly affect the concentration about 1 km downstream of the confluence.

Both these processes are, however, frequently encountered during the dilution and are responsible for changes in concentration and physico-chemical forms of radium sometimes extending far downstream from the mixing point. They are caused by a change in the composition of water containing radium which can occur in the mixing. On one hand, radium dissolved in waste water comes into contact with solid particles suspended in natural water and can adsorb on them. Because of the adsorption, concentration of dissolved radium sometimes rapidly decreases. For instance Pradel (1976) reported more than 70% decrease of dissolved radium in river water only 2 km below the discharge of uranium mine and mill effluents. Similar, although not so pronounced decrease was described by Tsivoglou et al. (1960), Iyengar et al. (1978) and De Jesus et al.(1980) . Kirchmann et al.(1973) found that the ratio of dissolved to particulate forms of radium in river water decreased with distance from the point where the river water was contaminated with waste waters containing mainly dissolved radium.

On the other hand, composition of water phase can be significantly changed by the mixing which can lead to a change in the dissolved forms of radium and/or to a change in the abundance and nature of particulate forms of radium. These effects are poorly documented for radium but their probability follows from common principles and from the possibility of radium release from sediments, discussed in the next paragraph. It is to be expected, for instance, that dilution of waste waters containing high percentage of radium in particulate forms with natural water will cause dissolution or desorption of radium from suspended solids resulting in a decrease in abundance of the particulate forms. This effect is difficult to detect as the decrease in abundance of the particulate forms is usually ascribed to their sedimentation. However, it can be sometimes traced from an increase in the absolute concentration of dissolved radium with distance from the discharge point (see for instance Iyengar et al., 1978) or from unexpectedly low effect of dilution on the concentration of dissolved radium.

The effect can explain why Justyn and Stanek (1968) found higher concentrations of radium in river water below discharge of waste waters than those calculated from mixing rule, or why Bouquieaux (1968) observed decrease in abundance of particulate forms of radium from 75-99% to 20% after dilution of water containing 1.6 $Bq.l^{-1}$ ^{226}Ra with uncontaminated river water. An evidence of dissolution and reprecipitation of particulate forms of radium induced by dilution has been given by Sebesta et al.(1981). The authors found an equilibrium distribution of radium and barium between dissolved and particulate forms to exist in mine drainage waters purified by precipitation of barium sulfate. The equilibrium distribution obeyed homogeneous distribution law valid for isomorphous coprecipitation of radium with barium sulfate (Benes and Majer, 1980). Soon after dilution of the purified waters with river water the distribution of both elements was significantly distorted, but the original distribution was restored 13 km downstream from the dilution point. The restoration could take place only due to recrystallization of barium-radium sulfate.

5.4.3. Migration in Natural Streams

5.4.3.1. Dissolved and particulate forms of radium in natural streams

There are two basic forms of radium migration in surface streams: migration in solution and migration in suspended solids. These migration forms, corresponding to dissolved and particulate radium , are closely interrelated and are obviously connected with bottom sediments of streams via sedimentation of suspended solids and resuspension of bottom sediments. Any advanced study of radium migration therefore has to involve differentiation between the dissolved and particulate forms of radium. Perhaps it is worthwhile to mention in this connection that filtration through filter paper is not suitable for such a differentiation as paper can adsorb significant amounts of dissolved radium (Erbacher and Nikitin, 1932).

(a) Mechanisms of interaction occurring during migration

The ratio of the migration forms of radium in streams is largely determined by the processes of adsorption of dissolved radium on stream suspended solids and by dissolution or desorption of radium from the solids. These processes were discussed in previous paragraph. Their kinetics and other quantitative characteristics are poorly known, since relatively few data are available on the changes observed in natural streams and even the existing data are sometimes difficult to interpret because of complicating effects of dilution and other natural processes. Precipitation of sparingly soluble radium compounds can be excluded as a process affecting radium migration in surface waters for the same reasons as already mentioned in paragraph 5.2.1. However, coprecipitation of radium with foreign solids is possible, for instance coprecipitation with ferric hydroxide is probable in river water receiving untreated mine drainage waters (Pradel, 1976).

(b) Nature of dissolved and particulate forms

Very few data exist on the nature of dissolved and particulate forms of radium in surface waters. Many authors have assumed that radium is dissolved in such waters only as hydrated cations Ra^{2+}, which is not correct in view of the presence of sulfates in most surface waters and, consequently, of the possible formation of radium sulfate ion pair (cf. 5.2.1.). Simple calculation suggests that the abundance of the ion pair can be significant ($>5\%$) in waters containing more than 43 $mg.l^{-1}$ free sulfates. Benes and Obdrzalek (1980) analyzed the dissolved forms of radium in little polluted river water and in river water contaminated with purified (by precipitation of $BaSO_4$ and sedimentation) uranium mine effluents. Radiotracer method in combination with free-liquid electrophoresis was employed. The results indicated presence of some electrophoretically immobile (neutral) forms in amounts exceeding maximum possible abundances of $RaSO_4$ ion pair. Very probably some organic complexes or radium were present whose abundances were $\geq 14\%$ in the unpolluted river and $\geq 11\%$ in the contaminated water.

Benes et al.(1980) analyzed particulate forms of radium in the same river water samples as indicated above using method of selective dissolution (Benes et al., 1981). Four different forms of particulate radium were distinguished: "loosely bound" (L.B.), "acid soluble" (A.S.), radium coprecipitated with barium sulfate ($BaSO_4$) and radium "in crystalline detritus (C.D.). The results shown in Table 5.IX. revealed that particulate radium was predominantly barium-radium sulfate in the river water contaminated with purified mine effluents. The same conclusion has been drawn for the same samples from other results (Sebesta et al., 1981). The bond of radium in solids suspended in the unpolluted river water was considerably different. The main form here was "acid soluble" form or radium "in crystalline detritus" indicating prevalence of radium adsorbed on natural solids or incorporated in insoluble rock particles, respectively.

From the point of view of further migration of radium it is important that the proportion of the "loosely bound" form of radium was very low. This form represented radium liberated with 0.1M solution of sodium chloride and its low abundance suggested that radium would not be easily redissolved from suspended solids of the given type due to an increase in ionic strength of surface water. The same particulate forms of radium were further characterized by electrophoretic method. Suspended solids carrying ^{226}Ra were labelled with radium 224 and their electrophoretic mobility was determined (Benes and Obdrzalek, 1980). The low electrophoretic mobility found indicated very low surface charge (zeta potential) of the solids.

5.4.3.2. Sedimentation and resuspension processes

Among the most important natural processes affecting migration of radium in streams belong sedimentation of suspended solids and resuspension of bottom sediments. Both the processes strongly depend on the velocity and turbulence of stream flow, and their relative importance for radium migration is proportional to radium content in suspended solids and in bottom sediments. Some information on the processes can be derived from general knowledge of factors affecting suspended load of streams. For instance Lerman (1979) described concentration of suspended solids in streams C as a function of river discharge Q using equation

$$\log C = \log A + m.\log Q$$

where m and A are constants highly varying from one river to another.

(a) Analysis of radium content in river bottom sediments

Importance of sedimentation for radium migration has been clearly demonstrated by a number of authors who found that radium content in river bottom sediments is strongly enhanced below the discharge of radium containing waters into a river (see, e.g., Tsivoglou et al., 1960, Pradel, 1976, Iyengar et al., 1978, U.S.EPA, 1979). Consequently, radium content in sediments has been suggested as a good indicator for water pollution with radium (Tsivoglou, 1963). Particularly the fine dispersed fractions of sediments are well suitable for this purpose (Mansfeld and Hanslik, 1980).

Several authors described a pronounced decrease in radium content of river bottom sediments with distance from the discharge point (see Table 5.X. and Iyengar and Markose, 1970, Parsont, 1967, Kirchmann et al., 1973, Sebesta et al., 1978, 1980, Kurokawa and Kurosawa, 1980b). Character of the decrease generally depends on the character of the river. In the areas of uniform velocity of river flow and in the absence of significant time variations in the flow rate (absence of flood scouring) the decrease tends to be monotonous, usually exponential (Parsont, 1967, Kurokawa and Kurosawa, 1980b). If, on the other hand, the stream velocity varies with distance due to varying character of the river, fluctuations in radium content of sediments can be observed (e.g. Marple and Zettwoog, 1980, Sebesta et al., 1980). All these findings are easily explainable in terms of common sedimentation principles (see for instance Lerman, 1979).

The irregular distribution of radium in river bed sediments along the river can also be due to resuspension, transportation and re-sedimentation of the sediments during high flow rates or floods. The scouring and transportation of sediments containing radium were detected in many places but are poorly understood. Their extent is rather site specific. For instance Parsont (1967) observed no significant movement of radium containing sediments in a creek system during periods of high flow rate which was reflected in the lack of seasonal variations in radium concentration in the sediments. On the other hand, Iyengar et al.(1978) found much higher contents of radium in river bed sediments before monsoon flood than after it (see Table 5.X.). Temporal variations of radium in sediments indicative of successive scouring and removal in flood flows were also detected in Shirley Basin area in Wyoming (U.S.EPA, 1979). A long range transportation of radium containing sediments has been reported by Tsivoglou (1963) and Pradel (1976).

The "leap frog" mechanism of radium transport in sediments is particularly important in arid areas where radium is concentrated in dry sedimentts during dry periods and resuspended and transported in floods (Australia, New Mexico, Wyoming - see Williams, 1976, U.S.EPA, 1979). The U.S. Environmental Protection Agency developed model pertaining for such a case which describes movement of radium in a river basin. Calculations using the model for conditions prevailing in Wyoming or New Mexico have shown that radium 226/228 dissolved in flood water due to scouring of the sediments would not exceed 0.26 $Bq.l^{-1}$.

(b) Analysis of data on radium concentration in river water

The sedimentation and resuspension processes can also be studied by analysis of data on radium concentration in river water. Either changes in the radium concentration with water flow rate at one site or changes along the stream can be evaluated. Although the analysis of some of available data is complicated by simultaneous effect of dilution and/or by uncertainty as to whether dissolved or total radium was measured, the data corroborate common rule that for a given system, increasing flow rate tends to diminish the sedimentation and to increase the resuspension. For instance Stanek (1973) found approximately linear increase in radium concentration in river water with increasing river flow rate at a river profile far downstream of discharge of uranium mine and mill effluents.

A number of authors described a decrease in radium concentration along a stream which could not be explained by dilution (Parsont, 1967, Justyn and Stanek, 1968, Hanslik and Mansfeld, 1973, Kurokawa and Kurosawa, 1980b, Sebesta et al., 1981). The decrease can be ascribed to sedimentation of particulate radium. Resuspension of sediments containing radium was first noticed by Tsivoglou et al. (1958) who found a direct relationship between suspended activity and stream flow rate.

Similar relationship is demonstrated in Table 5.XI. by data adopted from Hanslik and Mansfeld (1973) and Sebesta et al.(1981). The resuspension is also indicated by the downstream increase of radium concentration in river water during periods of high water flow (see Table 5.XI. and data by Iyengar and Markose, 1970).

The effect of sedimentation and resuspension can be most easily analyzed from the changes in the ratio of dissolved to particulate radium in water. As shown in Table 5.XI. the ratio decreases with increasing flow rate at a given site. Below certain ("critical") flow rate the ratio increases along the stream due to sedimentation of particulate radium. Above the critical value resuspension of bottom sediments prevails and the ratio decreases with distance. The critical value of flow rate without doubt depends on the character of stream and also on the amount of bottom sediment which accumulated at the given rate (confer the different ratios in Table 5.XI. at sites A and B and those measured several years apart at the same stream). The latter fact can also explain why for instance the ratio of dissolved to particulate radium found at the end of the spring high flow was substantially higher than that observed at the beginning of the spring flow or during a flash flood, although the flow rate was approximately the same (Benes et al., 1980). The reason lay in exhaustion of transportable radium-containing sediments after the prolonged high flow. It is interesting that the difference was accompanied at one site by a significant difference in the character of radium bond in suspended solids.

Because of many factors influencing it, the ratio of dissolved to particulate radium in streams considerably varies from time to time and from site to site (Hanslik and Mansfeld, 1973, Kirchmann et al., 1973, Sebesta et al., 1981). Values from 0.01 (for a small river receiving effluents from phosphoric acid plant - Bouquieaux, 1968) to 24 (for little polluted river - Kurokawa and Kurosawa, 1980b) have been reported. However, no distinct seasonal variations have been found except for the effect of river flow rate discussed above.

A closer analysis of the data presented in Table 5.XI. reveals that the concentration of dissolved radium in the river water little depends on flow rate, except for the lowest values of the flow rate. At higher flow rates the concentration increases along the stream, although no additional source of dissolved radium was present in the studied system. These findings point to redissolution of radium from resuspended bottom sediments, which counterbalances the effect of dilution and brings about the downstream increase in dissolved radium concentration. The redissolution was assumed already by Tsivoglou et al.(1960) who claimed that a large fraction of dissolved ^{226}Ra in Animas river downstream of uranium mill resulted from leaching of river bed deposits. Similarly, Iyengar et al. (1979) explained the comparatively high radium concentration in river waters during monsoon periods by solubilization of radium bound in sediments.

The redissolution of radium gives rise to the question how large quantities of radium can be released in this way. This problem has been studied by laboratory experiments and will be treated in paragraph 5.4.7. From the laboratory and field (New Mexico) data U.S.EPA(1979) concluded that only 10% of radium deposited in sediments will go back into solution in flood waters. The importance of the redissolution in nature is probably diminished by sediment burial and dilution. It can also be assumed that certain leachability limit exists, after reaching of which no more radium can be removed regardless of duration, frequency or intensity of agitation.

5.4.4. Migration in Water Reservoirs

Relative importance of sedimentation and resuspension processes is entirely shifted in favour of sedimentation in water reservoirs as compared with streams. Sedimentation of particulate radium in reservoirs can be strongly enhanced due to absence of larger streaming. It is therefore to be expected that average ratio of dissolved to particulate forms of radium in reservoirs will be higher than in streams. This assumption in supported for instance by data by Marple and Zettwoog (1980) who found this ratio more than three times higher in water reservoir than in river feeding the reservoir. Iskra et al.(1969) determined that the ratio varied from 27.3 to 2.0 in the case of radium added to lake water in a glass cylinder, depending on whether bottom sediments were absent or present, respectively. The results also indicated possible effect of water plants on the ratio.

Radium distribution and forms in reservoirs are probably more susceptible to seasonal changes due to stratification, upwelling and biologic effects, but experimental data demonstrating the changes are virtually missing. Possible effects of the mentioned processes on radium migration in reservoirs can be at least partially derived from the general theory of sedimentation in lakes treated comprehensively by Lerman (1979). The author quoted (p.367) unpublished data by Imbodena indicating a uniform distribution of radium with depth in a freshwater lake.

Natural resuspension of bottom sediments in deep reservoirs is very unlikely and therefore such sediments represent a nearly permanent sink for radium. A larger probability of radium release from sediments exists in shallow reservoirs (several meters deep), particularly in those characterized by a variable water level or by well developed water currents. Justyn (1973) compared radium concentrations at the inlet and outlet of a shallow pond contaminated with waste solids from uranium mine effluents and found about 10% release of radium from the pond. The release was dependent on scouring of sediments whose intensity increased with decreasing water level.

Stanek (1973) determined concentrations of radium in water and bottom sediments of a reservoir created by river dam. The variations in the concentrations along the reservoir profile from river inlet to dam outlet were rather low, the highest concentrations were found near the river inlet. The latter finding indicates partial sedimentation of radium in the reservoir. The average retention of riverborn radium in the reservoir found by the author was 18%. However, relative abundance of suspended forms of radium increased from 27% at the river inlet to 30% in the water leaving the reservoir (below the dam), which points to some complicating effect, probably to scouring bottom sediments in a vicinity of the near-bottom outlet of the dam.

5.4.5. Migration in Estuaries

Very little data have been published about the behaviour of radium in estuarine waters. Results by Chan and Li (1979) seem to indicate that radium behaves similarly to other cationic elements during the mixing of river waters with saline sea water, i.e. that it undergoes desorption from suspended solids. The desorption is due to the competition of cations contained in sea water for the same adsorption sites on the surface of solids or due to an enhanced solubility of solids containing radium in changing water environment.

5.4.6. Migration in Bottom Sediments

This paragraph will briefly discuss migration processes of radium in, into and from bottom sediments undisturbed by water currents, i.e. in the absence of any significant scouring of the sediments. General theory of the migration of elements in bottom sediments and across the sediment-water interface pertaining to such a case has been given by Lerman (1979). It can be derived from the theory that radium behaviour in bottom sediments may be characterized by the following factors and processes:

1) Nature and composition of the sediment are primary factors determining migration of radium. Particle-size distribution and particle shapes of the sediment affect its porosity, which is commonly between 70 and 90% in surface layers and decreases to 40-60% in deeper layers (Lerman, 1979). Water contained in the pores (the pore or interstitial water) represents the main migration medium. Its composition is significantly influenced by the composition of sediments.

2) Radium undergoes adsorption and desorption processes largely determining its distribution between the pore water and the sediments. The distribution depends also on the composition of the pore water, which can substantially differ from the composition of water overlying the sediment layer.

3) Chemical reactions involving organic matter and minerals, like decomposition of organic matter, reduction of sulfate to sulfide, dissolution and precipitation of mineral phases etc. can bring about desorption/dissolution of radium into pore water or adsorption/coprecipitation of radium from the pore water.

4) Existence of concentration gradient in the pore water can cause diffusional flux of radium which in combination with the adsorption/desorption and coprecipitation/dissolution processes leads to a redistribution of radium throughout the sediment layer.

5) Higher or lower concentration of radium in sediment pore water relative to the overlying water can establish conditions for diffusional flux that results in the release of radium from the sediment layer or in the concentration of radium from the overlying water to sediments, respectively.

6) Sediment deposition rate, which can vary from milimeters per 1000 yr in the pelagic ocean to centimeters per year in lakes, man-made reservoirs and near-shore oceanic areas, significantly affects probability of radium release from the sedimentts as it determines the rate of burial of deeper sediment layers.

7) Groundwater inflow to a stream or reservoir can bring about an upward flow of sediment pore water and release of radium from sediments, significant in case of a continuing dissolution or desorption of radium from sediments to the pore water.

8) Activity of bacteria and benthic organisms (generally confined to the upper few centimeters of the sediment column) may affect radium migration due to radium uptake by these organisms, to their effect on the chemical reactions in sediments or to bioturbation of sediments.

The relative importance of these factors and processes for radium migration remains little documented by field data. There exists only an indication that the vertical redistribution of radium in sediment column (ad 4) is rather slow: several authors reported that radium discharged to surface waters contaminated only the surficial layers of sediments (Justyn, 1973, Stanek, 1973, Kirchmann et al., 1973, Kribek et al., 1979). Stanek (1973) studied vertical migration of radium in sediment layers taken from bottom sediments of river dam and placed in glass cylinder in the same sequence as was that in the dam. Some of the experiments were carried out with addition of ^{226}Ra into the top layer. Both the "labelled" and unlabelled experiments led to the conclusion that the downward migration of radium was very slow. For instance only 3.6% of the radium added to the homogenized top 20 cm of the sediments migrated in one month to the 20-30 cm layer and 1.6% to the 30-40 cm layer. Some additional information can be obtained from studies of radium interaction with sediments, discussed in the following paragraph.

Mathematical models similar to those describing the groundwater migration of radium can also be construed for migration in bottom sediments (Lerman, 1979). However, the complicated nature of the migration and scarceness of input data pertaining for radium make usability of such models very problematic.

5.5. DISTRIBUTION OF RADIUM BETWEEN WATER AND FRESHWATER SEDIMENTS

5.5.1. Different Approaches for Studying Interaction of Radium With Freshwater Sediments

In view of the well established importance of sediments for radium migration in surface waters a number of authors tried to obtain data characterizing interaction of radium with freshwater sediments. The efforts have been directed towards investigation of uptake (mainly adsorption) of radium by sediments and release (desorption or dissolution) of radium from sediments. Some of the data obtained were discussed above, other investigations were based on the analysis of correlation between radium contents in natural sediments and composition or other properties of the sediments. However, major part of the investigations has been carried out by laboratory experiments. Two general approaches have been adopted:

1) investigation of radium distribution between natural water or aqueous solution and natural sediments;
2) study of radium distribution between water phase and model solids representing components of natural sediments.

Principal advantage of the second approach lies in simpler interpretation of the distribution but data obtained in this way can usually serve only as complementary for data characterizing natural sediments.

Distribution of radium between water phase and sediment can be influenced by the following factors:

- duration of contact between water and sediment,
- ratio of volume of water to the amount of sediment (liquid/solid ratio or V/m),
- composition and granulometric properties of sediment,
- composition of water phase,
- nature of radium bond in sediment.

For the discussion of the effects of these factors it is worthwhile to distinguish between studies concerned with uptake and release of radium.

5.5.2. Studies Concerned With Uptake of Radium by Sediments

Uptake of radium by sediments can proceed by several mechanisms: adsorption of radium on the surface of sediment particles, coprecipitation of radium with foreign solids coating the surface of sediment particles, incorporation of radium into components of sediment during their recrystallization and biological uptake of radium by organisms living in sediment. Relative importance of these mechanisms is little known, as most studies carried so far were confined to rather simple investigation of radium distribution between water and sediments as a function of several main factors. More can be expected in this respect from a detailed study of the distribution and particularly from the analysis of radium bond in sediments, for instance by the method of selective dissolution (Sebesta et al., 1980).

5.5.2.1. Quantifying solid-liquid interactions

Laboratory studies of radium uptake by sediments have dealt mainly with radium adsorption as can be seen from rather rapid kinetics of radium uptake in well mixed systems, reflected in uptake of more than 90% of the "equilibrium" value during the first 10 min. - 2h contact (Hanslik and Mansfeld, 1973, Stanek, 1973, Mansfeld, 1977). Biological uptake and incorporation by recrystallization would be probably much slower processes, coprecipitation from artificially prepared solutions or from natural water can mostly be excluded in laboratory experiments. Hanslik and Mansfeld (1973) and Mansfeld (1977) found that kinetics of radium adsorption on sediments depends on pretreatment of sediment. Drying of sediments generally slowed down the subsequent adsorption but the effect was rather low. Furthermore, moderate effects of sediment particle size and of liquid/solid ratio on the kinetics were noted.

The liquid/solid ratio (V/m) has again been identified as a primary factor affecting the extent of radium adsorption by sediments (Hanslik and Mansfeld, 1973, Mansfeld, 1977, Mansfeld and Hanslik, 1980). The effect of V/m on ionic adsorption is generally expressed using relation

$$K_D = (m_a/m_s).V/m$$

where m_a and m_s are amounts of radium adsorbed and remaining in solution, respectively, and K_D is distribution constant. Consequently, many authors used K_D also for characterization of radium distribution between water and solids (see 5.3. and Stanek, 1973, U.S.EPA, 1979, Marple and Zettwoog, 1980). However, the effect of V/m on radium adsorption by sediments is not simple, as demonstrated in Table 5.XII. It can be seen that the distribution constant K_D increases with increasing V/m.

From the inconstancy of K_D value pertaining to one type of sediment, Mansfeld (1977) concluded that the distribution constant K_D is not suitable parameter for characterizing adsorption properties of sediments for radium. In a thorough study of radium adsorption on 25 different river sediments the author came to the conclusion that for each sediment certain maximum percentage of radium adsorption (A_{max}) exists which cannot be exceeded by further decreasing V/m. He suggested to express the effect of V/m on percentage of radium adsorption (A) by sediments using adsorption isotherm

$$m/VA = K/A_{max} + m/VA_{max}$$

where K is a constant (equal to m/V at A = 0.5 A_{max}). By a statistical analysis of available data the author corroborated validity of the isotherm and concluded that A_{max} and K are parameters well suitable for characterization of the ability of sediments to adsorb radium. Alternatively, modified distribution constant can be used for the same purpose, defined as (Mansfeld and Hanslik, 1980)

$$K_D = A.(A_{max}-A)^{-1}.V.m^{-1}.$$

The values of K found for 25 river bed sediments lay in the range from 14.8 to 2866 $mg.l^{-1}$, K_D varied between 360 and 17400 $cm^3.g^{-1}$for 5 river sediments.

Statistical analysis of available data revealed significant correlation between parameter K and content of fine fraction in the studied sediments (Mansfeld, 1977). Dependence of K (in $mg.l^{-1}$) on percentage abundance in sediment of particles smaller than 0.1 mm ($F_{0.1}$) was described by equation

$$K = (0.0012\ F_{0.1} + 0.0081)^{-1}.$$

This finding agrees well with data characterizing relation between radium content in fractions of natural sediments and granulometric properties of the fractions. Parsont (1967), Hanslik and Mansfeld (1973) and Sebesta et al.(1978, 1980) found that fine fractions of river bed sediments contained more radium per gram than coarser fractions of the same sediments. Consequently, radium is concentrated mainly in fine fractions in accordance with common rule that adsorption per gram increases with increasing specific surface area of adsorbent. Shearer and Lee (1964) reported an independence of radium content of sediment particle size for river sediments contaminated with uranium mill waste solids. Reason for this difference probably lies in the different mechanism of sediments contamination.

5.5.2.2. Role of the nature of sediments

Little is known about the effect of composition of sediments on their ability to adsorb radium. Mansfeld (1977) came to the conclusion that no significant correlation exists between this ability, expressed via parameter K, and content of organic matter in 25 different sediments. Similar conclusion was drawn by Justyn and Stanek (1968) and Sebesta et al.(1980) from data on radium content in river bed sediments and on percentage weight loss by ignition of the sediments. In contrast, Parsont (1967) found direct relationship between the radium and organics contents.

Several authors tried to elucidate the effect of sediment composition by analysis of radium adsorption on model substrates representing individual components of sediments. Kribek et al.(1979) studied adsorption of radium on ferric hydroxide, which is an important component of sediments in waters receiving mine effluents. It has been found that the adsorption ability of ferric hydroxide is larger than that of soils but it decreases with the age of ferric hydroxide. Benes et al.(unpublished results) compared adsorption of radium on ferric hydroxide, kaolinite, quartz sand and silica in a broad range of conditions and concluded that the adsorption increases in the order

kaolinite > ferric hydroxide > quartz sand > silica at pH 6

and

ferric hydroxide > kaolinite ~ quartz sand ~ silica at pH 8.

An extensive study of this type was carried out by Mansfeld and Hanslik (1980). Table 5.XIII. presents data by the authors characterizing adsorbability of radium on 8 minerals. It has been found that the order of minerals according to their ability to adsorb radium is different for distilled water and tap water, which was explained by different effect of ions present in tap water on radium adsorption by different substrates.

5.5.2.3. Influence of water composition

Data shown in Tables 5.XII. and 5.XIII. demonstrate that radium adsorption on sediments can be significantly affected by water composition. In accordance with common principles (see e.g. Benes and Majer, 1980), it is to be expected that increasing salinity of water will reduce radium adsorption, particularly if polyvalent cations are present. The effect of pH may also prove significant. For instance adsorption of radium on ferric hydroxide strongly depends on pH in the pH region 6-8 (Benes et al., unpublished results). Stanek (1973) studied radium adsorption on lake sediments from lake water whose pH value was adjusted with hydrochloric acid or ammonium hydroxide to 1-10. The highest adsorption was found at pH 3-5, significant decrease was observed towards the extreme values of pH. Mansfeld (1977) did not find any substantial effect of pH on radium uptake by river sediments in the pH region 5-7.

5.5.3. Studies Concerned With Release of Radium From Sediments

Although several attempts have been made to study desorption of radium preliminary adsorbed in laboratory on river bed sediments or their components (Hanslik and Mansfeld, 1973, Stanek, 1973, Benes et al., unpublished results), most of experimental studies dealt with release of radium already present in natural sediments.

5.5.3.1. Kinetics of releases

It has been shown that kinetics of the radium release from wet sediments is rapid, an equilibrium being reached in less than 20 min.(Hanslik and Mansfeld, 1973, Stanek, 1973, Sebesta et al., 1978). Preliminary drying of sediments tends to slower down the kinetics (Sebesta et al., 1978). Intensity of agitation has been shown to have only a small effect on the kinetics of radium release, the "equilibrium" amount of radium that can be released little depends on temperature in the range of 10-20°C(Stanek, 1973). Shearer and Lee (1964) detected no increase in the leachability of radium as a result of grinding of river sediments.

5.5.3.2. Equilibrium solid-liquid and natural conditions

In natural stream conditions sediments are in contact with flowing water whose radium content can significantly change with time. In order to model the situation when a sediment is continuously brought into contact with fresh portions of water having low radium content (model of stream leaching of sediments), release of radium during consecutive contacts of one portion of sediment with several fresh portions of water was investigated. Shearer and Lee (1964) reported a moderate decrease in the radium release in three consecutive leachings with distilled water from river bed sediments contaminated with uranium mill waste solids. Sebesta et al. (unpublished results) found that no substantial change occurred in the percentage of radium leached from sediments contaminated with $Ba(Ra)SO_4$ with number of consecutive leachings up to 10 except for the first three steps (V/m ratio during the leachings was 731-899 $cm^3.g^{-1}$).

Data obtained by Hanslik and Mansfeld (1973) on the cumulative release of radium preliminary adsorbed on river bed sediment are shown in Fig. 5.9. Constant V/m ratio was used, equal to 25 $cm^3.g^{-1}$. As can be seen the course of the release can be roughly predicted using a suitable distribution constant. The authors suggested using K_D obtained from desorption experiments for calculating minimum time or water volume necessary for total radium desorption from river bed sediments after cessation of radium discharge into river. It must be kept in mind, however, that the release of radium contained in natural sediments can significantly differ from the desorption of radium preliminary adsorbed on the same sediments. For instance Stanek (1973) found about twice as large percentage desorption of radium additionally adsorbed on a lake sediment as the release of radium contained in the sediment. The difference was also reflected in K_D values which were equal to 520-890 $cm^3.g^{-1}$ for the former case and to 1150-1770 $cm^3.g^{-1}$ for the latter case.

Fig.5.9 represents graphical illustration of the possible effect of the liquid/solid ratio on radium desorption from sediments. Similar demonstration of the effect of V/m on radium leaching from river bed sediments is given in Fig.5.10, where relative amount of radium leached is seen to linearly increase with the liquid/solid ratio. Sebesta et al.(1978) explained this fact by dissolution of barium-radium sulfate contained in the sediment.

5.5.3.3. Effect of composition of sediments

An important role in the release of radium undoubtedly belongs to the composition of sediments. However, data illustrating the role are scarce (see, e.g., difference between the results reported by Shearer and Lee, 1964, Stanek, 1973, and Sebesta et al., 1978, who worked with different sediments). Justyn and Stanek (1968) observed easier release of radium from sediments containing 8% of organic matter than from those with only 1% of organic matter. Benes et al.(unpublished results), in a study of radium desorption from model components of river sediments, found that radium adsorbed on ferric hydroxide can be desorbed with 0.01 M sodium chloride solution more easily than radium adsorbed on quartz sand.

5.5.3.4. Effect of composition of water phase

Effect of composition of water phase on the release of radium from sediments was studied by several authors. According to Tanner (1964) extractability of radium from sediments is aided by the following factors:

1) pH value of water low enough to dissolve alkaline earth carbonates;
2) availability of chelate agents for dissolution of other metallic coatings in which radium is trapped;
3) presence of other cations in sufficient concentration to displace radium adsorbed on sediments.

Shearer and Lee (1964) found that the addition of monovalent and bivalent cations in 0.01 molar concentrations to water enhanced leachability of radium from river sediment. The effect of cations increased in the order $KCl < HCl < CaCl_2 < SrCl_2 < BaCl_2$, which was explained by the authors as due to increasing ability of the cations to exchange with radium bound in the sediment. An essentially linear relationship has been observed between the amount of radium leached and barium cloride concentration in the range 0.001-0.015 molar. Stanek (1973) studied desorption of radium from lake sediments as a function of pH of lake water, adjusted by addition of acid or hydroxide to 1-10. The desorption passed through a single maximum at pH 3-4.

Data characterizing the effect of water composition on leachability of radium from bed sediments of a river receiving uranium mine effluents purified by precipitation of barium sulfate have been reported by Sebesta et al.(1978) . From the data, shown in Table 5.XIV., follows entirely different sequence of the effect of cations on radium leachability than that found by Shearer and Lee (1964). This difference as well as other differences discussed above very probably arises from different nature of radium bond in the sediments used for the investigation.

Sebesta et al.(1980) studied radium bonding in river bed sediments using method of selective dissolution. The results indicated that the main form of radium in sediments affected by discharge of purified mine waters was $Ba(Ra)SO_4$, which was formed during purification of mine waters and sedimented in river. Abundance of this form decreased with distance from the discharge point but irregularly, showing a maximum in a site where river flow was slow. The latter finding suggests that the fraction of sediments containing $Ba(Ra)SO_4$ was rather fine. The second most important form of radium in the sediments was soluble in 1 molar hydrochloric acid and probably represented radium adsorbed on the surface of sediment particles. This form prevailed in sections of the same river little affected by waste waters or receiving radium mainly in dissolved form.

The data presented in Table 5.XIV. were obtained with the river sediment affected by the discharge as mentioned above. It has been postulated that radium release from such sediment is to a great part determined by dissolution of $Ba(Ra)SO_4$. This hypothesis has been checked by simultaneous study of radium liberation from artificially prepared barium-radium sulfate (see Table 5.XIV.). The amount of $Ba(Ra)SO_4$ roughly corresponded to its content in the sediments. It can be seen that the sequence of leachabilities of $Ba(Ra)SO_4$by different electrolytes is similar to that found with natural sediments, although the values differ to some extent. The differences may be either due to some screening effect in the sediments or due to a significant effect of release of other forms of radium from the sediments.

5.6. CONCLUSION AND RECOMMENDATIONS

Water is undoubtedly the most important agent in transporting, concentrating and dispersing of radium on the earth. Our knowledge of radium behaviour in the hydrosphere is still very imperfect. The many gaps existing in the knowledge have been shown above. As the knowledge is important not only from purely scientific reasons but especially for practical purposes of protection of the environment and of radiation dose assessment, it is necessary to fill in the gaps in our knowledge by further investigation of the factors and processes influencing radium migration in aquatic environments. In this connection use has to be made of all pertinent physico-chemical and geochemical laws. It must also be emphasized that a substantial progress can be achieved only if most advanced analytical methods are employed. These methods have to involve a sufficiently detailed analysis of the physico-chemical forms of radium in water and relevant solids. Development of such methods belongs to the foremost tasks for the future research.

As regards the radium migration itself, further studies are needed particularly of the following problems:

1) uptake and release of radium by freshwater suspended solids and bottom sediments - field and laboratory studies of the effect of basic factors and of the mechanism of both processes;

2) character of radium bond in freshwater suspended solids and bottom sediments - dependence on the type of solid and water;

3) effect of sedimentation on radium deposition in bottom sediments and on properties of the sediments - field studies of the relation between composition of suspended solids and bottom sediments, kinetics of sedimentation, stratification of sediments, etc.;

4) transport of radium-containing bottom sediments in streams via resuspension and resedimentation - field investigation of main effects: type of stream, type of sediment, water flow rate, seasonal variations, etc.;

5) leaching of radium from mill tailings, mine spoils and gypsum piles in relation to climatic conditions and pile state - field studies of the effects of weathering, erosion, revegetation, etc.

6) effect of radium bond in waste solids and bacterial oxidation on leachability of radium from the solids - laboratory studies using method of selective dissolution;

7) groundwater migration of radium released during conventional and in situ (solution) mining of uranium ores - field studies;

8) effect of radium speciation on movement of radium in porous media: seepage in tailings dam, migration in aquifers and soil profiles - laboratory and field studies;

9) interaquifer migration of radium injected or seeped into ground waters.

TABLE 5.I. COMPOSITION OF WATER PHASE IN ACID AND ALKALINE LEACH URANIUM MILL TAILINGS POND*

Component	Acid leach	Alkaline leach
Dissolved Ra (Bq.l^{-1})	1.4 - 178	1.3 - 74
SO_4 (mg.l^{-1})	2000 - 50000	1500 - 4300
Cl "	10 - 3700	100 - 400
HCO_3 "	0	1100$^+$
CO_3 "	0	4600$^+$
Ba "	0.1 - 1	-
Ca "	100 - 700	10$^+$
Fe "	0.5 - 5000	0.1 - 0.5
Mg "	1500 - 5000	10$^+$
Mn "	0.4 - 4500	0.15$^+$
Na "	25 - 19000	3000 - 4300
NH_4 "	69 - 500	4.4$^+$
pH (untreated raffinate)	2.1 - 4.1	9.6 - 10.8

* based on data reported by Tsivoglou and O'Connell (1964), U.S. EPA (1979) and Levins (1979).

\+ data based on one sample only

TABLE 5.II. COMPOSITION OF WATER FROM URANIUM MINES

Component	Mining waters	Drilling waters	Purified waters
Total Ra ($Bq.l^{-1}$)	0.3 - 113	0.007 - 24	0.004 - 11
Dissolved Ra (%)	11 - 97	97 - 99*	2 - 17** 81 - 99+
Total Ba ($mg.l^{-1}$)	0.05 - 0.80	0.08 - 0.30*	0.17 - 8.4
Dissolved Ba (%)	35 - 79*	92 - > 93*	4 - 5** 40 - > 89+
Ca ($mg.l^{-1}$)	10 - 300	24+	1 - 158
Fe "	0.5 - 21	0.1 - 1.5*	0.1 - 3.3
Mg "	5 - 49	7 - 9*	0.5 - 47
Na "	5 - 500	1.0 - 4.6	39 - 360
Cl "	0.5 - 358	2.1 - 3.2	49 - 238
HCO_3 "	20 - 400	89 - 99*	82 - 160
SO_4 "	10 - 935	< 5 - 144	17 - 1045
Suspended solids ($mg.l^{-1}$)	2.6 - 3000	1 - 9	1 - 145
pH	6.4 - 8.6	6.4*	3.9 - 8.3

* data for one specimen only

** mining water purified by coprecipitation with barium sulfate

\+ drilling water purified with cation exchange resin

TABLE 5.III. CONCENTRATIONS OF RADIUM-226 IN LEACHATE AND QUANTITY LEACHED FROM ABANDONED TAILINGS (in Bq.l^{-1} and Bq, Bryant et al., 1979)

Consecutive leaching periods (months)	Tailings* Equivalent flow rate (mm/month)		Tailings + sediments** Equivalent flow rate (mm/month)	
	41	460	411	460
1	2.7	4.0	5.1	4.5
3	3.9	4.8	6.7	3.0
3	4.7	4.9	12.6	2.8
Total amount leached	52.7	971.2	96.6	648.5

* 90 kg

** 80 kg tailings + 10 kg Ba(Ra)SO_4 sediment

TABLE 5.IV. CONCENTRATIONS OF RADIUM-226 IN LEACHATE AND QUANITY LEACHED FROM FRESH TAILINGS (in Bq.l^{-1} and Bq, Bryant et al., 1979)*

Consecutive leaching periods (months)	Untreated tailings	Chemically fixed tailings	Tailings + sludge + vegetation	Fixed tailings + sludge + vegetation
1	3.1	< 0.04	3.0	0.48
2	3.1	0.07	8.3	0.33
2	1.8	0.07	4.6	0.37
Total amount leached	57.6	~ 0.7	113.6	10.4

* Total volume of leachate, 17.2 l - 25.2 l, equivalent volume of tailings, 200 l.

TABLE 5.V. MAXIMUM AMOUNTS OF RADIUM-226 LIBERATED FROM 3 g OF URANINITE ORE WITH 30 ml OF SOLUTION OF VARIABLE COMPOSITION*

Leaching solution	Percent Ra-226 liberated from ore containing	
	3.1 Bq.g^{-1}	20.0 Bq.g^{-1}
distilled water	3.6	0.7
0.001M HCl	4.4	1.3
0.1MHCl	4.5	2.9
0.001M NaOH	2.3	1.1
1M KCl	31.	22.
0.1M KCl	15.	5.7
0.01M KCl	9.	2.6
0.01M NaCl	3.1	2.3
0.01M LiCl	1.7	-
0.01M $MgCl_2$	1.3	0.8
0.01M $CaCl_2$	1.9	0.6
0.01M $SrCl_2$	0.3	0.3
0.01M $BaCl_2$	0.3	0.6
0.1M $BaCl_2$	0.3	0.1
1M $BaCl_2$	0.3	0.1

* data published by Havlik et al., (1968), corresponding to the maximums found on the time course of the leaching

TABLE 5.VI. PERCENTAGE OF RADIUM ISOTOPES LEACHED FROM MONAZITE AS A FUNCTION OF LEACHING SOLUTION COMPOSITION (LAZAREV, 1959)

Solutions	Isotope	Concentration of salt (M)	Composition of salt NaCl	KCL	$BaCl_2$
Neutral	^{224}Ra	0.01	0.05	0.20	1.26
"	"	0.1	0.23	0.56	1.29
"	"	0.5	0.42	0.91	1.17
"	"	1.0	0.45	0.90	1.32
"	"	$1.5 - 4.0^+$	0.81	1.18	1.12
Acidic (0.05M HCl)	"	0.01	2.1	2.2	2.6
"	"	0.1	2.5	2.8	2.6
"	"	1.0	2.9	2.9	3.0
"	"	$1.5 - 4.0^+$	2.6	2.7	2.7
"	^{226}Ra	0.01	5.2	5.6	6.3
"	"	0.1	5.4	7.1	6.6
"	"	1.0	6.0	7.1	8.1
"	"	$1.5 - 4.0^+$	6.3	7.4	-

* particle size, < 0.25 mm, liquid/solid ratio, 40 $l.kg^{-1}$, contact time, 9h

\+ 1.5M for $BaCl_2$, 3.0M for KCl and 4.0M for NaCl

TABLE 5.VII. MONITORING OF GROUNDWATER CONTAMINATION IN A VICINITY OF A TAILINGS POND (IYENGAR et al., 1979)

Monitoring year	^{226}Ra ($Bq.l^{-1}$)	SO_4 ($mg.l^{-1}$)	Cl ($mg.l^{-1}$)	Hardness ($mg.l^{-1}$)
Well adjacent to tailings pond				
1st	0.017	155.7	206.9	885.0
2nd	0.017	816.4	312.5	1232.
3rd	0.017	614.4	295.3	1172.0
4th	0.018	1245.0	390.0	1410.0
Well 500 m away from tailings pond				
1st	0.015	125.0	199.1	790.5
2nd	0.016	970.7	319.1	1180.5
3rd	0.015	509.3	309.4	853.6
4th	0.016	1158.0	384.7	1380.0

TABLE 5.VIII. CHECK OF VALIDITY OF MIXING RULE FOR MIXING OF RADIUM IN WASTE WATER WITH RIVER WATER (SEBESTA et al., 1981)*

Sampling date	Dissolved ^{226}Ra measured	calculated	Particulate ^{226}Ra measured	calculated
76-10-25	0.13	0.13	0.70	0.70
76-11-22	0.24	0.19	1.29	1.18
77-01-06	0.35	0.16	2.22	1.85
77-02-17	0.13	0.15	1.22	1.41
77-03-15	0.11	0.11	0.78	1.04
77-05-17	0.13	0.18	1.48	1.26
mean value	0.18±0.04	0.15±0.01	1.28±0.22	1.24±0.16

*concentrations in $Bq.l^{-1}$, mixing ratio 1:2 - 1:3

TABLE 5.IX. DISTRIBUTION OF RADIUM 226 (IN %) AMONG FORMS DISTINGUISHED BY SELECTIVE DISSOLUTION OF SOLIDS SUSPENDED IN RIVER WATER (BENES et al., 1980)

Water sample*	Radium form	Sampling date 78-03-06	79-04-18	79-07-30
A	L.B.	< 0.1	3.	3.9
A	A.S.	40.7	5.	55.3
A	$BaSO_4$	25.4	17.	26.3
A	C.D.	33.9	75.	14.5
B	L.B.	0.1	0.3	0.1
B	A.S.	8.0	9.2	13.6
B	$BaSO_4$	87.9	84.2	79.8
B	C.D.	4.0	6.3	6.5
C	L.B.	0.1	0.9	0.6
C	A.S.	15.4	19.5	11.4
C	$BASO_4$	84.3	72.6	81.3
C	C.D.	0.2	7.0	6.7

*A - little polluted river water upstream of confluence with wastewater channel;

B - river water 1 km downstream of the confluence with wastewater channel conveying uranium mine effluents purified by precipitation of barium sulfate and subsequent sedimentation;

C - river water 13 km downstream of the confluence.

TABLE 5.X. RADIUM CONCENTRATIONS (IN Bq.l^{-1}) IN BOTTOM SEDIMENTS OF PERIYAR RIVER AT ALWAYE, INDIA (IYENGAR et al., 1978)

Sampling place	Pre-monsoon		Post-monsoon	
	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra
Ferry, 1.3 km upstream of Alwaye	0.12	0.04	0.09	0.00
Industrial outfall area	11.84	1.50	0.42	0.08
Ferry, 0.3 km downstream of Alwaye	0.98	0.13	0.22	0.10
Methanam, 1.8 km downstream of Alwaye	0.17	0.01	0.06	0.24

TABLE 5.XI. EFFECT OF FLOW RATE (IN $m^{-3}.s^{-1}$) ON THE CONCENTRATION (IN Bq.l^{-1}) OF DISSOLVED AND PARTICULATE RADIUM 226 IN RIVER WATER RECEIVING PURIFIED URANIUM MINE EFFLUENTS

Flow rate at site A*	Dissolved		Particulate		Diss./particul.	
	Site A	Site B	Site A	Site B	Site A	Site B
0.77 (1)	0.27	0.16	0.10	0.06	2.77	2.67
1.07 (1)	0.07	0.10	0.07	0.07	0.96	1.39
1.33 (1)	0.05	0.07	0.02	0.11	2.18	0.66
1.97 (1)	0.11	0.14	0.16	0.26	0.66	0.54
3.00 (1)	0.08	0.13	0.15	0.40	0.56	0.32
3.45 (1)	0.07	0.10	0.19	0.50	0.40	0.19
3.90 (1)	0.07	0.09	0.31	0.57	0.23	0.16
0.91 (2)	0.21	0.20	1.42	0.52	0.15	0.59
1.23 (2)	0.12	0.21	1.00	0.70	0.12	0.30
2.09 (2)	0.18	0.17	2.96	1.11	0.06	0.15

*Site B was ~ 12 km downstream of the site A, increase of flow rate between A and B did not exceed 24%

(1) calculated from data by Hanslik and Mansfeld (1973).

(2) calculated from data by Sebesta et al., (1981).

TABLE 5.XII. EFFECT OF LIQUID/SOLID RATIO AND BARIUM IONS ON RADIUM ADSORPTION BY SEDIMENTS (MANSFELD, 1977)*

V/m ($cm^3.g^{-1}$)	$c_{Ba^{2+}}$ (molar)	Adsorption (%)	K_D ($cm^3.g^{-1}$)
10	10^{-5}	93.7	149
50	"	81.9	225
500	"	42.8	374
10	10^{-4}	91.1	103
50	"	70.3	118
500	"	42.2	365
10	10^{-3}	77.7	35
50	"	48.4	47
500	"	12.8	73

* little contaminated river bed sediment, particle size < 2mm, solution for adsorption prepared from distilled water, original concentration of ^{226}Ra in the solution 740 $Bq.l^{-1}$

TABLE 5.XIV. LEACHING OF RADIUM (IN %) FROM RIVER BED SEDIMENTS AND BARIUM-RADIUM SULFATE (SEBESTA et al., 1978).

Leaching solution	Wet sediment	Dry sediment	$Ba(Ra)SO_4$
0.01M HCl	31.1	28.6	13.6
0.01M $CaCl_2$	15.8	13.0	13.5
0.01M KCl	8.5	6.4	-
0.01M NaCl	5.1	3.6	10.9
0.01M $BaCl_2$	1.2	2.3	0.3

* leaching time 1 h, 450 cm^3 of leaching solution, 0.5 g of sediment, 10 mg of $Ba(Ra)SO_4$

TABLE 5.XIII. DATA CHARACTERIZING ADSORPTION OF RADIUM ON MODEL COMPONENTS OF RIVER BED SEDIMENTS (MANSFELD AND HANSLIK, 1980)*

Substrate	K (mg.l^{-1})	A_{max} (%)	K'_D (cm^3.g^{-1})
	Distilled	water	
Quartz	346	95.6	3020 ± 290
Feldspar	34	95.6	13400 ± 8500
Calcite	584	93.1	1730 ± 90
Dolomite	60	95.8	23700 ± 5200
Kaolinite	29	96.4	61800 ± 29700
Biotite	34	97.3	33200 ± 5800
Bentonite	3.4	98.1	393000 ± 84000
Phlogopite	165	98.1	8100 ± 2200
	Tap	water	
Quartz	2021	79.3	480 ± 200
Feldspar	1187	95.7	670 ± 60
Calcite	8333	84.4	96 ± 10
Dolomite	362	98.6	2300 ± 170
Kaolinite	7009	95.2	139 ± 21
Biotite	138	99.7	6660 ± 620
Bentonite	277	73.8	2710 ± 600
Phlogopite	604	97.2	1370 ± 170

* explanations of symbols see in text, particle size of all substrates was less that 0.1 mm

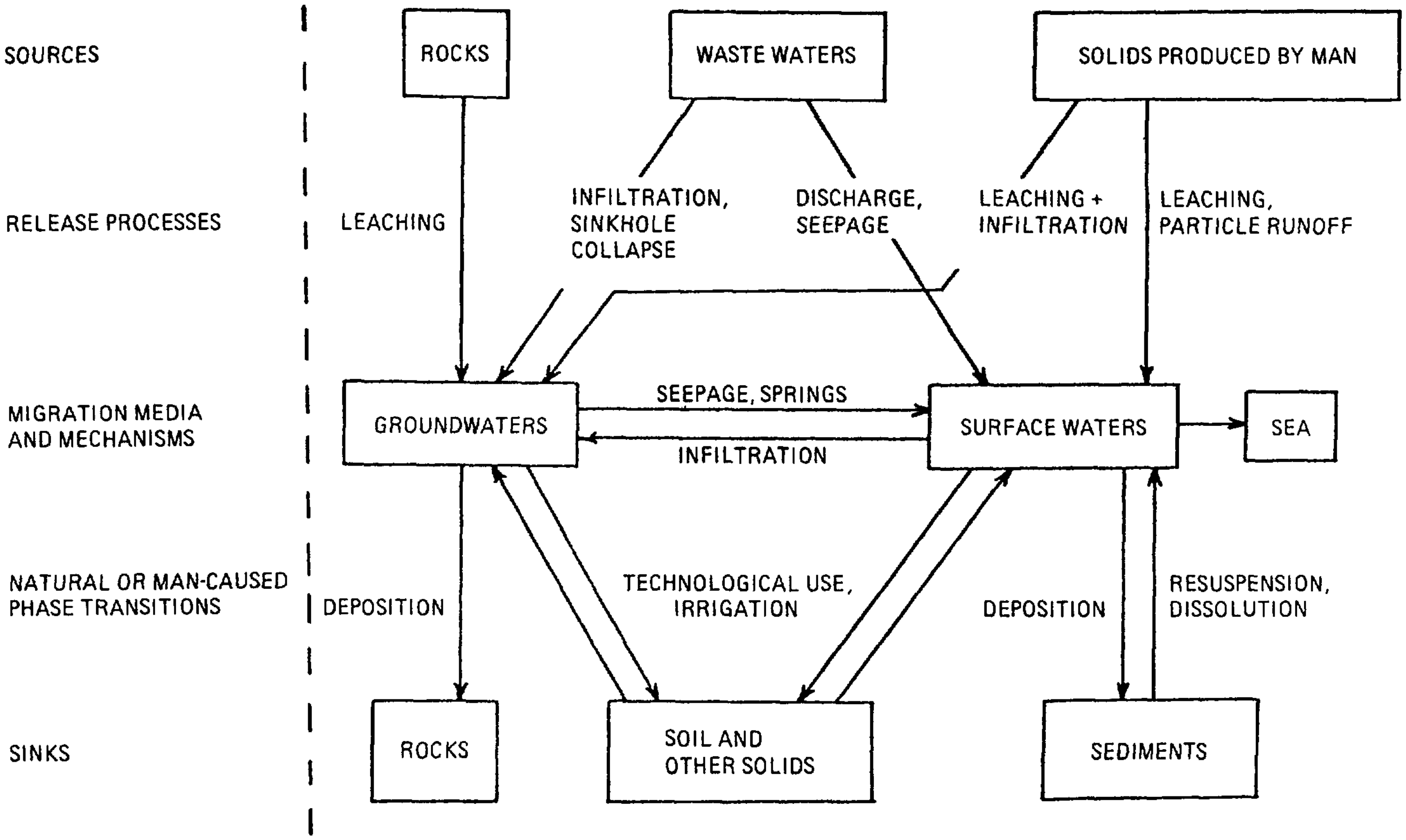

Fig. 5.1. Migration pathways of radium in inland waterways and aquifers.

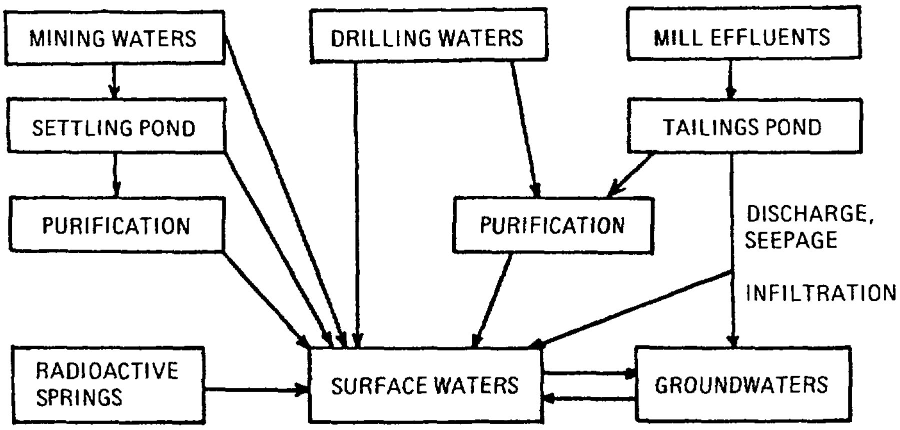

Fig. 5.2. Migration pathways of radium from radioactive wastewaters and springs to surface and ground waters.

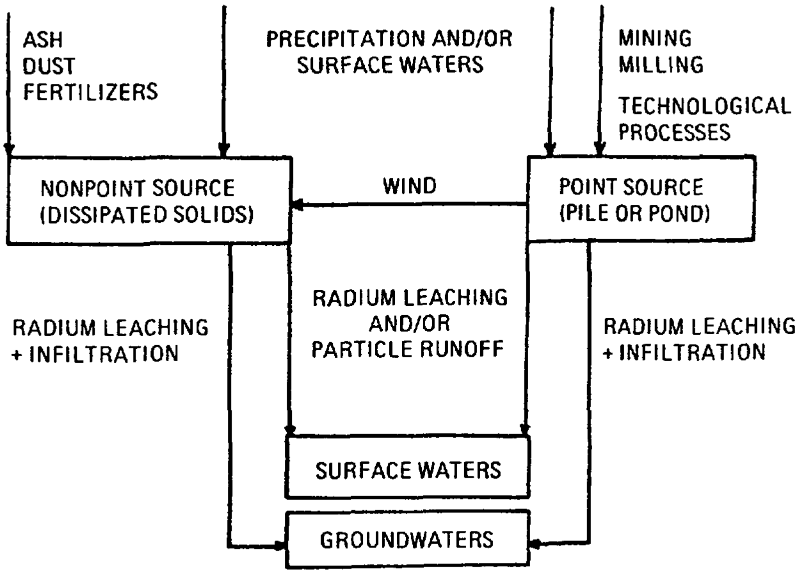

Fig. 5.3. Migration pathways of radium from solids produced by man to surface and ground waters.

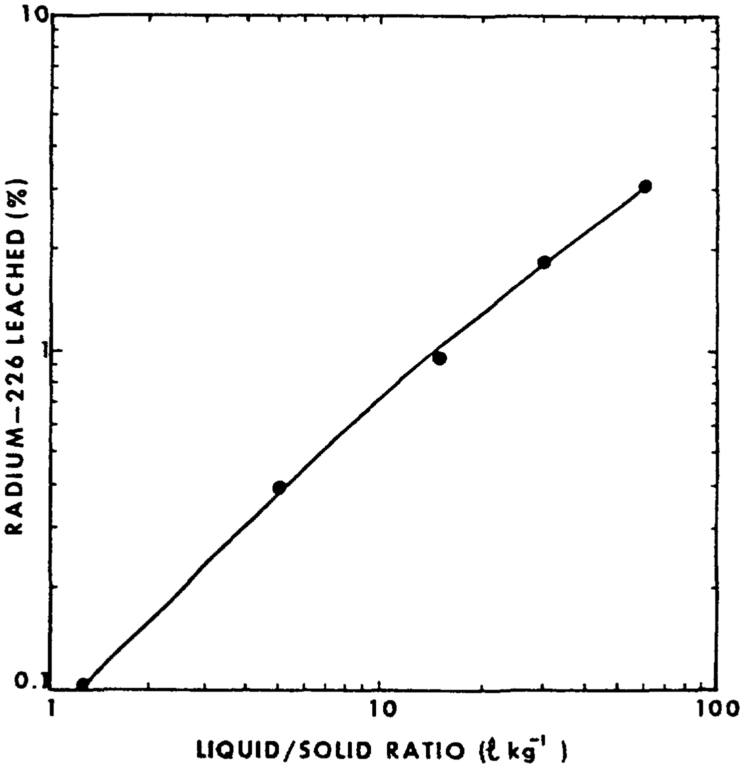

FIG. 5.4. Effects of solid/liquid ratio on leaching of radium-226 from uranium mill tailings. Contact time, 3h, pH of leachate, 4.4-5.1, temperature, 25°C. (Reprinted from Levins et al., 1978, by permission of the author).

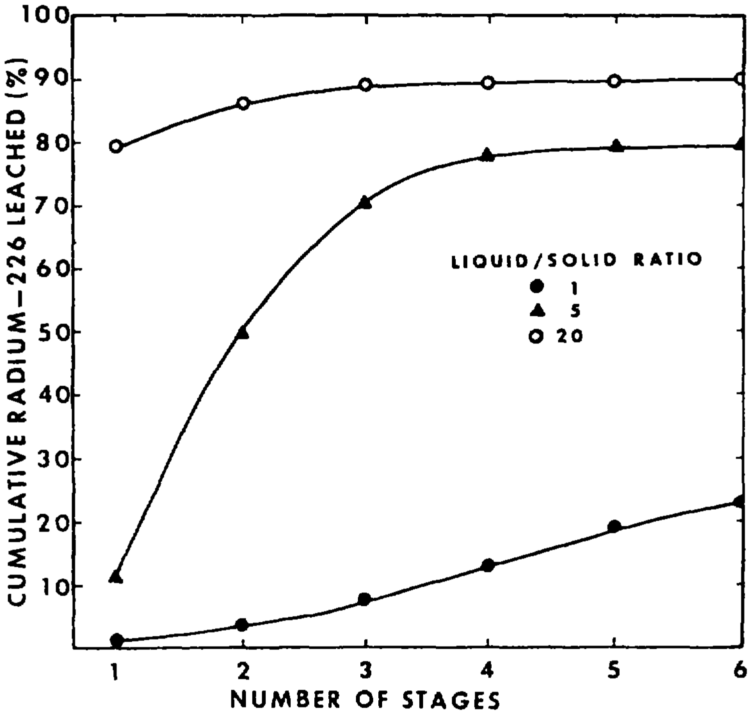

FIG. 5.5. Repetitive leaching of radium-226 from uranium mill tailings with 1M NaCl. Contact time, 0.5 h, pH of leachate, 3.8-5.2, temperature, 25°C. (Reprinted from Levins et al., 1978, by permission of the author).

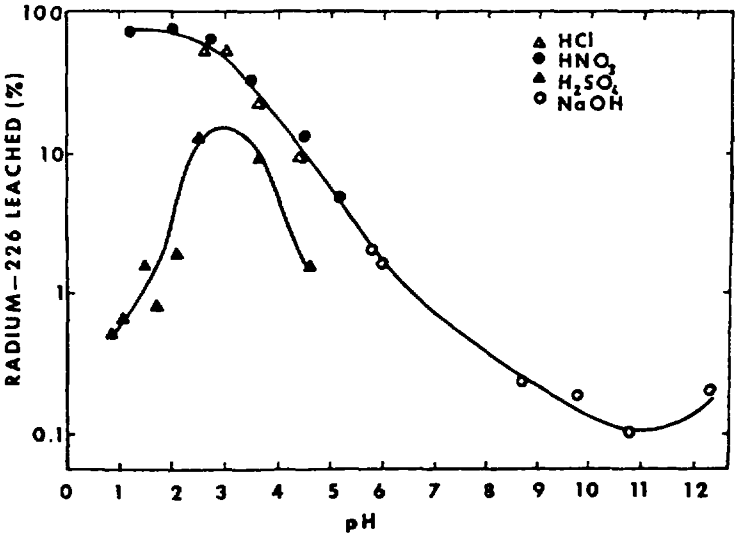

FIG. 5.6. Effect of pH on leachability of radium-226 from uranium mill tailings. Leaching solution, demineralized water with added acid or hydroxide, liquid/solid ratio, 30 $l \cdot kg^{-1}$, contact time, 1.5 h, temperature, 25°C. (Reprinted from Levins et al., 1978, by permission of the authors).

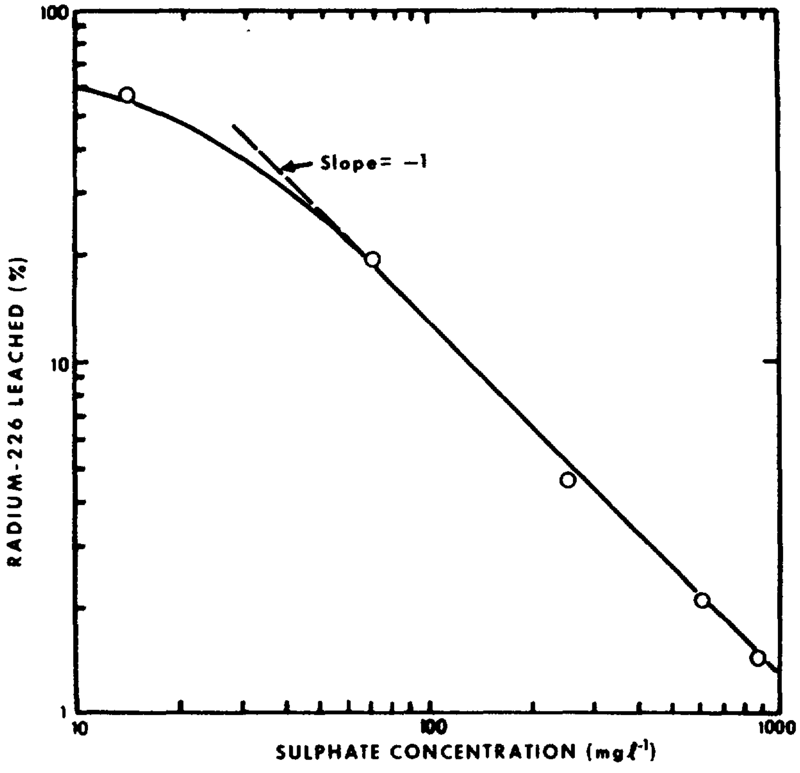

FIG. 5.7. Effect of sulfate concentration on leaching of radium-226 from uranium mill tailings with 1M NaCl. Contact time, 1 h, liquid/solid ratio, 5 $l \cdot kg^{-1}$, pH 4.0-4.6, temperature, 24°C. (Reprinted from Ryan and Levins, 1979, by permission of the authors).

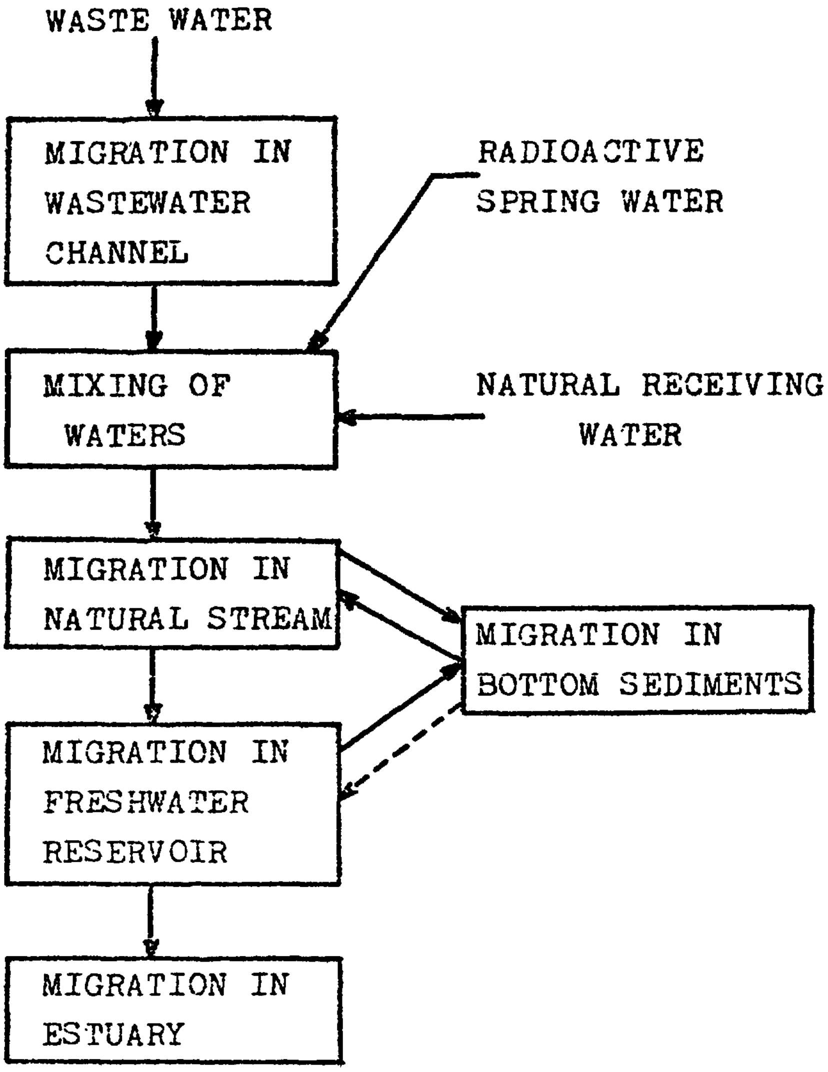

Fig. 5.8. Block scheme of radium migration in surface waters.

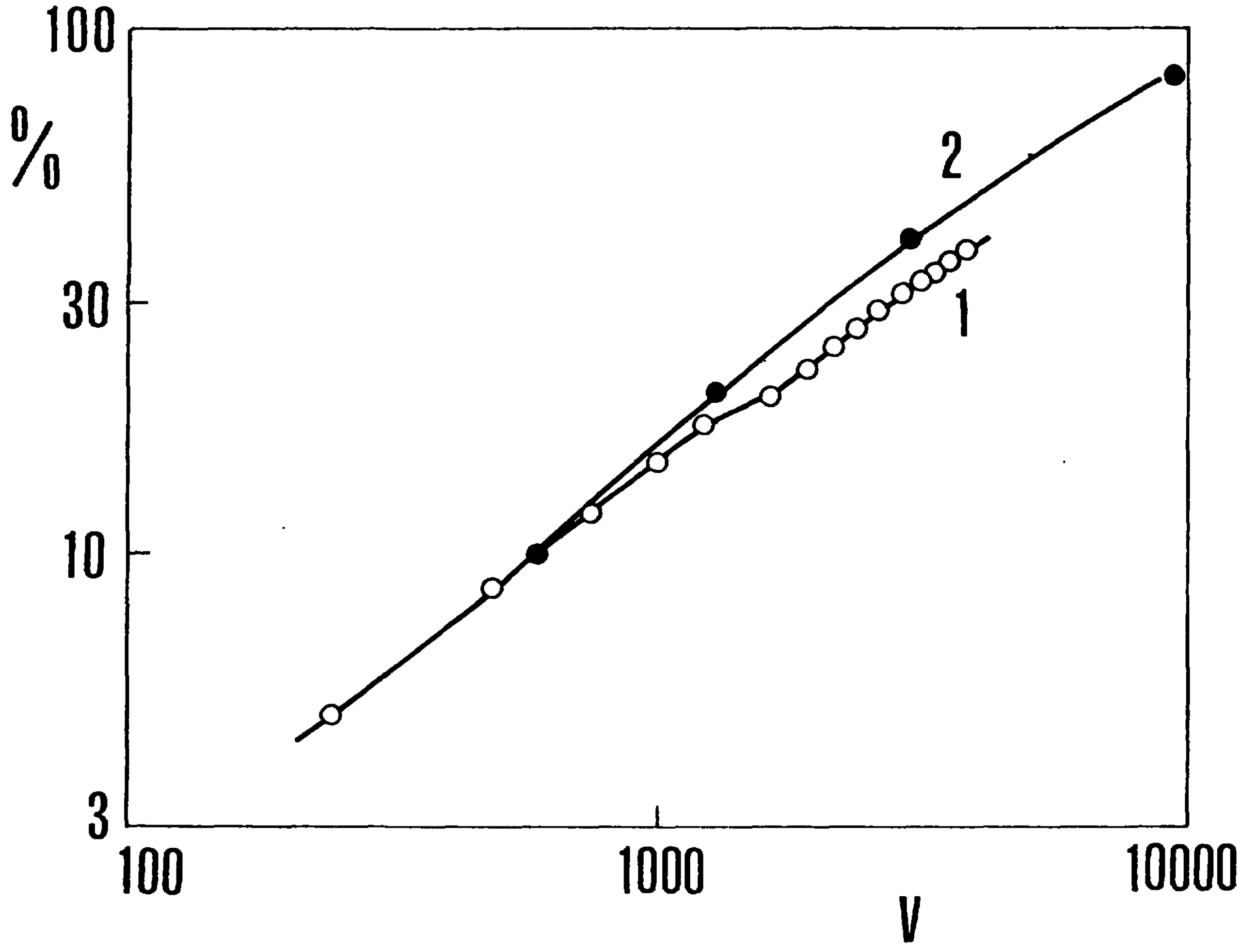

FIG. 5.9. Cumulative desorption of radium (%) preliminary adsorbed on river bed sediment as a function of total (cumulative water) volume V (in cm^3): 1 - experimental data for 24 h desorption from 10 g of sediment by uncontaminated river water; 2 - equilibrium desorption calculated assuming K_D = 576 $cm^3.g^{-1}$.
(From Hanslik and Mansfeld, 1973, by permission of the authors).

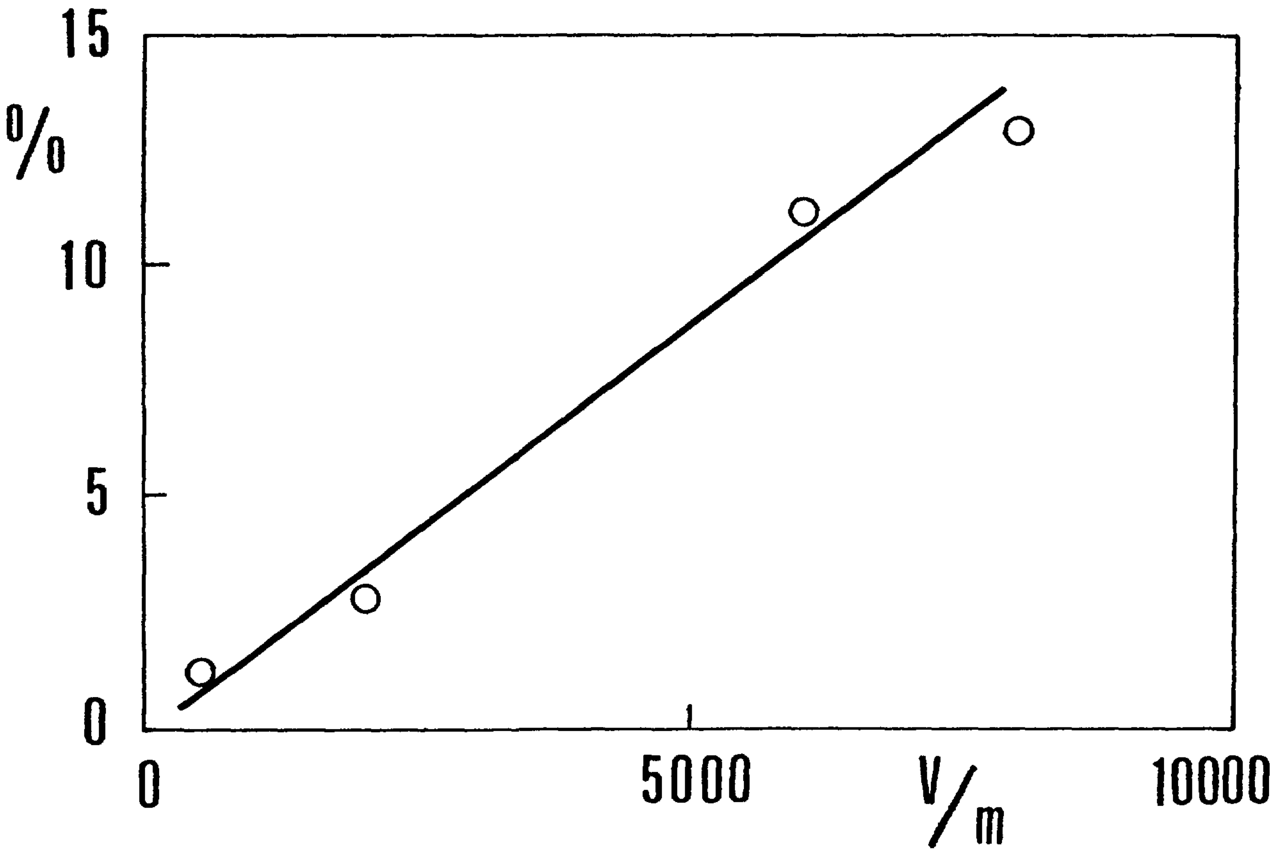

FIG. 5.10. Effect of liquid/solid ratio (in $cm^3.g^{-1}$) on radium leaching (%) with distilled water from river bed sediments contaminated with $Ba(Ra)SO_4$ from purified uranium mine drainage waters.
Leaching time 1 h, sediment contained 13.1 $Bq.g^{-1}$ Ra-226.
[From Sebesta et al., (1980), by permission of the authors].

REFERENCES

BAKHUROV V.G., et al., Radioactive Wastes of Uranium Plants (in Russian), Atomizat, Moscow (1965)

BELOUSOVA I.M., SHTUKKENBERG J.M., Natural Radioactivity (in Russian) MEDGIZ, Moscow (1961).

BENES P., MAJER V., Trace Chemistry of Aqueous Solutions, Elsevier, Amsterdam (1980).

BENES P., OBDRZALEK M., The use of radiotracer method for analysis of the state of radium in waste and surface waters (in Czech), Proceedings of the Seminar "Hydrochèmia '80," Water Research Institute, Bratislava (1980) 139.

BENES P., et al., Study of the state and behaviour of radium in surface and waste waters (in Czech), Proceedings of the IX. Conference on Radionuclides and Ionizing Radiation in Water Technology, CSVTS, Liberec (1978) 99.

BENES P., et al., Analysis of the suspended forms of radium and barium in surface waters using the method of selective dissolution (in Czech), Proceedings of the Seminar "Hydrochèmia '80," Water Research Institute, Bratislava (1980) 157.

BENES P., et al., Method of selective dissolution for characterization of particulate forms of radium and barium in natural and waste waters, Water Res., 15 (1981) 1299.

BENES P., et al., The physicochemical forms of traces of radium in aqueous solutions containing chlorides, sulfates and carbonates, Radiochem.Radioanal. Letters, 50 (1982) 227.

BOENZI D., et al., A Study on the Sorption in the Lake Bracciano Region (Rome), Comitato Nazionale Energia Nucleare, Rome (1965).

BOUQUIAUX J., Redissolution du radium insoluble d'origine rèsiduaire dans un fleuve, Trib. CEBEDAU 21 291 (1968) 66.

BRYANT D.N., et al., Leachability of Radioactive Constituents from Uranium Mine Tailings, Status Report, Environmental Protection Service, Environment Canada, EPS4-WP-79-4 (1979).

CHAN L.H., LI Y.H., Desorption of Ba and ^{226}Ra from river-borne sediments in the Hudson estuary, Earth Planet. Sci. Lett. 43 3 (1979) 343.

DE JESUS A.S.M., et al., Movement of Radium from South African Gold/Uranium Mine Dumps into the Aqueous Environment, Progress Report to the International Atomic Energy Agency, Pelindaba, South Africa (1980).

DLOUHY Z., Movement of Radionuclides in the Aerated Zone. Report to the IAEA, Vienna (1967).

EADIE G.G., KAUFMANN R.F., Radiological evaluation of the effects of uranium mining and milling operations on selected ground water supplies in the Grants Mineral Belt, New Mexico, Health Physics 32 (1977) 231.

ERBACHER O., NIKITIN B., Bestimmung der Loeslichkeit von Radiumsulfat in Wasser bei 20°, Z. Physik. Chem. 158A 3/4 (1932) 216.

GARRELS R.M., "A Survey of low temperature water - mineral relations", Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology, International Atomic Energy Agency, Vienna (1976) 65.

GUIMOND R.I., WINDHAM S.T., Radioactivity Distribution in Phosphate Products, By-products, Effluents and Wastes, U.S.EPA Technical Note ORP/CDS-75-3 (1975).

GUREGHIAN A.B., A Two-Dimensional Finite Element Solution for the Simultaneous Transport of Water and Solutes through a Non-homogenous Aquifer under Transient Saturated Unsaturated Flow Conditions, Permeability and Groundwater Containment Transport Symposium, Philadelphia (1979).

HANSLIK E., MANSFELD A., Natural Radionuclides in the System of Mine Waters, Their Distribution and Mutual Relations (in Czech), Final Report S-R-30-263, Water Research Institute, Prague (1970).

HANSLIK E., MANSFELD A., Investigation of Trends in Radioactive Contamination in Selected Streams (in Czech), Final Report No. R-502004, Water Research Institute Prague (1973).

HAVLIK B., et al., Radium-226 liberation from uranium ore processing mill waste solids and uranium rocks into surface streams-I,II, Health Phys. 14 (1968) 417, 423.

ISKRA A.A., et al., On the behaviour of natural radioactive elements in stationary water reservoir (in Russian), Atomnaya Energiya 27 2 (1969) 134.

IWASAKI I., Distribution of radium (^{226}Ra) in hot springs and evolution mechanism of radioactive springs (in Japanese), Onsen Kogakkaishi 7 1 (1969) 16.

IYENGAR M.A.R., MARKOSE P.M., Monitoring of the aquatic environment in the neighbourhood of uranium mill at Jaduguda, Bihar, Proc. of National Symposium on Radiation Physics, Trombay (1970) 473.

IYENGAR M.A.R., et al., Radium in natural and processing areas and its impact on human environment, Status Report to the IAEA Research Contract No. 1788/RB (1978, 1979).

JUSTYN J., Investigation of processes affecting the content and behaviour of natural radionuclides in water reservoirs. I. Reservoir Horka (in Czech), Final Report, Water Research Institute, Prague (1973).

JUSTYN J., STANEK Z., Investigation of streams contamination by natural radioactive substances (in Czech), Final Report No. S-R-30-238/4, Water Research Institute, Prague (1968).

KAMATH P.R., et al., "The changing radiation environment", Symposium on the Natural Radiation Environment, II, Rice University, Houston (1972).

KANROJI Y., et al., Geochemical study on the occurence of Ra and Rn in Shirahama Spa (in Japanese), Onsen Kagaku 29 4 (1979) 175.

KAUFMANN R.F., BLISS J.D., Effects of phosphate mineralization and the phosphate industry on Radium-226 in ground water of Central Florida, U.S.Environmental Protection Agency Report EPA/520-6-77-010, Las Vegas (1977).

KAUFMANN R.F., et al., Effects of uranium mining and milling on ground water in the Grants Mineral Belt, New Mexico, Ground Water 14 5 (1976).

KIRCHMANN R., et al., Etude du cycle biologique parcouru par la radioactivité, Report BLG 477, Centre d'Etudes Nucléaires de Mol, Bruxelles (1973).

KLUTE A., HEERMANN D.F., Water Movement in Uranium Mill Tailings Profiles, U.S.EPA Technical Note ORP/LV-78-8 (1978).

KOBAL I., Determination of ^{226}Ra in surface and drinking water, Progress Report to the IAEA Research Contract No. 1700/RB (1978).

KRIBEK B., et al., Sorption of radionuclides on natural sorbents, (in Czech), Final Report No. P-09-125-012-7/4, Faculty of Natural Science, Charles University, Prague (1979).

KUROKAWA Y., KUROSAWA R., Elution of uranium and radium from uranium ores to rain water, IAEA Meeting on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers, Vienna (1980a).

KUROKAWA Y., KUROSAWA R., Movement and deposition of radium in model river, IAEA Meeting on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers, Vienna (1980b).

LAZAREV K.F., Methods of determination of limiting leachability of radioelements from minerals (in Russian), Radiokhimiya 1 5 (1959) 603.

LERMAN A., Geochemical Processes. Water and Sediment Environments, Wiley-Interscience, New York (1979).

LEVINS D.M., et al., Leaching of radium from uranium tailings, Proceedings of OECD/NEA Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico (1978) 271.

LEVINS D.M., Environmental impact of uranium mining and milling in Australia, Presented at the Ninth Annual Hydrometallurgical Meeting, Canadian Institute of Mining and Metallurgy, Toronto (1979).

LYNN R.D., ARLIN Z.E., Anaconda successfully disposes uranium mill waste water by deep well injection, Mining Eng. 14 7 (1962) 49.

MANSFELD A., Natural radionuclides in waters, their occurence and behaviour (in Czech), Ph.D. Thesis, Institute of Chemical Technology, Prague (1977).

MANSFELD A., HANSLIK E., The effect of mining radioactive raw materials on the quality of surface waters (in Czech), Final Report No. C16-331-112-03-04, Water Research Institute, Prague (1980).

MANSFELD A., ZAJICEK V., An Investigation of the radioactivity of potable water sources (in Czech), Final Report No. S-R-30-238/5, Water Research Institute, Prague (1969).

MARPLE M.L., ZETTWOOG P., Environmental pathways of Radium-226 in French regions of uranium mining and milling, Presented at the IAEA Meeting on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers, Vienna (1980).

MISAWA H., et al., "Solid and liquid wastes at the Ningyo-Toge Mine", Radiological Health and Safety in Mining and Milling of Nuclear Materials, IAEA Proceeding Series (1964).

MIYAKE Y., et al., "Content of uranium, radium and thorium in river waters in Japan", The Natural Radiation Environment (ADAMS J.A.S., LOWDER W.M. Eds), Rice University, Houston (1964) 219.

MROST M., LLOYD P.J., Bacteria oxidation of Witwatersrand slimes, Report IAEA-SM-135/32 (1971).

O'CONNELL M.F., KAUFMANN R.F., Radioactivity associated with geothermal waters in the Western United States, U.S. Environmental Protection Agency Technical Note ORP/LV-75-8A, Las Vegas (1976).

PARSONT M.A., The Distribution of ^{226}Ra in Aquatic Environment, Ph.D. Thesis, Colorado State University (1967).

PHILLIPS C.R., NATHWANI J.S., Rates of leaching of radium from contaminated soils: an experimental investigation of radium bearing soils from Port Hope, Ontario, Water Air Soil Pollut. 9 4 (1978) 453.

POSOKHOV E.B., Formation of Chemical Composition of Ground Waters (in Russian), Gidrometeorol. Izd., Moscow (1969).

PRADEL J., French Contribution to the IAEA Panel on the Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers, Mortagne (1976).

RAHN P.H., MABES D.L., "Seepage from uranium tailings ponds and its impact on ground water", Proc. Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, NEA, Albuquerque (1978).

ROY A.C., KELLER W., Water Pollution in the Serpent River, Status Report, Ontario Ministry of the Environment, Toronto (1976).

RUBINSKY E.I., Thickened discharge - a new approach to tailings disposal, Canad. Mining Metal. Bull. (December 1975) 47.

RYAN R.K., LEVINS D.M., "Extraction of radium from uranium tailings", Ninth Annual Hydrometallurgical Meeting, Canadian Institute of Mining and Metallurgy, Toronto (1979).

SCHLIEKELMAN R.J., Determination of radium removal efficiencies in Iowa water supply treatment processes, U.S. Environmental Protection Agency, Technical Note ORP/TAD-76-1, Washington (1976).

SCOTT R.C., BARKER F.B., Data on uranium in radium in ground water in the United States, U.S. Geological Survey Professional Paper 426 (1962).

SEBESTA F., et al., Studies on the source, distribution, movement and deposition of radium in inland waterways and aquifers, Progress Report of the IAEA Research Contract No. 1729/RB, Technical University of Prague (1978, 1980).

SEBESTA F., et al., Behaviour of radium and barium in a system including uranium mine waste waters and adjacent surface waters, Environ. Sci. Technol. 15 1, 71 (1981).

SHEARER S.D., Jr., LEE, G.F., Leachability of radium-226 from uranium mill solids and river sediments, Health Phys. 10, 217 (1964).

SHINPAUGH W.H., et al., Radiological survey of the inactive uranium-mill tailings at Tuba City, Arizona, Report ORNL-5450 (1980a).

SHINPAUGH W.H., et al., Radiological survey of the inactive uranium - mill tailings at Naturita, Colorado, Report ORNL-5454 (1980b).

SHUKTOMOVA I.I., et al., Forms of ^{226}Ra in soil horisons with its high concentration (in Russian), Pochvovedenie 2, 18 (1978).

SILLEN L.G., MARTELL A.E., Stability Constants, Special Publication No. 17, The Chemical Society, London (1964).

STANEK Z., Investigation of processes affecting content and behaviour of natural radionuclides in water reservoirs (Brno-Dam Reservoir) (in Czech), Final Report No. R-606001, Water Research Institute, Prague (1973).

STARIK I.E., Principles of Radiochemistry (in Russian), Publishing House of the Academy of Sciences of the USSR, Moscow (1959)., Chapter 1. English translation, U.S.AEC Report AEC-tr-6314 (1964).

STARIK I.E., LAZAREV K.F., On the form of uranium and thorium atoms in radioactive minerals (in Russian), Radiokhimiya 1 1, 60 (1959).

STARIK I.E., LAZAREV K.F., Effect of crushing of minerals on leachability of radioactive elements (in Russian), Radiokhimiya 2 6, 749 (1960).

TANNER A.B., "Physical and chemical controls on distribution of radium-226 and radon-222 in ground water near Great Salt Lake, Utah", The Natural Radiation Environment (ADAMS J.A.S., LOWDER W.M., Eds), Rice University, Houston 253 (1964).

TOKAREV A.N., SHCHERBAKOV A.V., Radiohydrology (in Russian), Gosgeoltekhizdat. Moscow (1956). English Translation, U.S. AEC Report AEC-tr-4100 (1960).

TSIVOGLOU E.C., Research for the control of radioactive pollutants, J.Water Pollut.Control Fed. 35 2, 242 (1963).

TSIVOGLOU E.C., O'CONNELL R.L., Nature, volume and activity of uranium mill wastes, International Atomic Energy Agency Report STI/PUB/78, Vienna (1964).

TSIVOGLOU E.C., et al., Effect of uranium ore refining wastes on receiving waters, Sew. Industr. Wastes 30 8, 1012 (1958).

TSIVOGLOU E.C., et al., Control of radioactive pollution of the Animas river, J.Water Pollut. Control Fed. 32 3, 262 (1960).

U.S.EPA, Reconnaissance study of radiochemical pollution from phosphate rock mining and milling, U.S. Environmental Protection Agency, Denver (1973).

U.S.EPA, Water quality impacts of uranium mining and milling activities in the Grant Mineral Belt, New Mexico, U.S. Environmental Protection Agency Report EPA 906/9-75-002, Dallas (1975).

U.S.EPA, Potential health and environmental hazards of uranium mine wastes, U.S. Environmental Protection Agency, Draft Report, Washington (1979).

WHITE D.E., et al., "Chemical composition of subsurface waters", Data of Geochemistry (FLEISCHER M., Ed.), Chapter F, Geological Survey Professional Paper 440-F, U.S. Government Printing Office, Washington (1963).

WILLIAMS A.R., The Movement of Radium in the Sub-coastal plains of Northern Australia, Presented at the IAEA Panel on the Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers, Mortagne (1976).

WUKASCH M.C., COOK L.M., Environmental surveillance in South Texas, Paper Presented at the Symposium on the Natural Radiation Environment Rice University, Houston (1972).

ZABORENKO K.B., et al., Study of the emanation and leaching of radium isotopes from monazite (in Russian), Radiokhimiya 1 6 (1959) 738.

ZETTWOOG P., Migration des radioéléments solubles des boues résiduaires des usines de traitement des minerais d'uranium au travers d'une barrière géologique, Commissariat à l'Energie Atomique, Rapport Interne SPT n° 182 (1980).

Chapter 6

BIOLOGICAL UPTAKE AND TRANSPORT

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6.1. INTRODUCTION

All aquatic organisms that have so far been studied appear to accumulate radium above its concentration in water. That is, the concentration factor (F) exceeds unity

$$F = \text{Bq kg}^{-1} \text{ fresh weight/Bq kg}^{-1} \text{ water.}$$

The reason for this and the mechanism by which it occurs are dealt with in the first section of this chapter; subsequent sections deal with the quantitative description of radium uptake and transfer.

6.2. THE MECHANISM OF RADIUM UPTAKE

From the chemical properties of the elements it can be predicted that radium may be taken up by cells via the same mechanism as calcium and the other alkaline earth elements (Mg, Sr, Ba). If this is the case, then there should be evidence of radium uptake across membranes and/or its distribution within tissues which can be correlated with that of calcium.

This appears to be the case for animals. In man, for example, 99% of the body calcium is distributed in the skeleton. The relative proportions of other elements are: Sr - 99%, Pb - 92%, Ba - 91%, P - 90%, Ra - 87%, Mg - 58%, but all other natural elements have lower propertions in the skeleton (ICRP 1975). Fish have a high proportion of body radium in the skeleton (e.g. Anderson et al. 1963); freshwater mussels accumulate Ra together with Ca, Mg, Ba, Mn, Fe and P in granules that are dispersed throught their body and, on the whole-body basis, the radium concentration is positively correlated with Ca and Ba concentrations but not correlated with the Mg concentration (Jeffree, Australia). For plants, there is a somewhat different but less well documented situation. Among 40 samples of aquatic and semi-aquatic macrophytes representing 19 species, Williams (Australia) found that the Ra distribution was not significantly correlated with that of Ca, Mg, Na, Cu, Zn, Fe or S but was positively correlated with that of Mn; among 18 samples of five organs (lamina, petiole, fruit, peduncle, rhizome), from a single species, Nymphaea gigantea, Ra distribution was not correlated with that of Ca, Mg, Na, Zn, U or S but was positively correlated with that of K and P. For terrestrial plants, the data of Smith (1971 a,b) show that the distribution of Ra is least like that of Ca among the alkaline earth elements, but any similarity between radium and other elements is still open to question. There is enough evidence to suggest that radium may behave differently in plants, so the matter should be further investigated.

Another way of investigating the mechanism of radium uptake is to examine its transfer through foodchains. If radium is taken up as if it were calcium, then it should be evenly distributed with calcium in the foodchain, and the observed ratio O.R. (O.R. = Ra:Ca ratio in one trophic level / Ra:Ca ratio in the preceding trophic level) would be unity. However, if cells can distinguish Ra from Ca, then the observed ratio ought to be less than unity, because calcium is a major nutrient and Ra is a non-nutrient.

In terrestrial soil-plant transfer, the observed ratio ranges from 0.05 (Kirchmann et al. 1968) to 0.5 (Bhujbal et al. 1970). In wetland plants, Williams (Australia) found an observed ratio of 0.06. In reference man the observed ratio is 0.015 (ICRP 1975). In terrestrial herbivores such as sheep, an observed ratio of ~ 0.1 can be inferred (Brownscombe et al. 1978). Unfortunately, the necessary dietary data for aquatic animals are lacking. However, in a summary of the available data on radium in the human foodchain, Williams (1981) found that among 9 generalized trophic-level transfers in the aquatic links of the chain, 8 showed a decrease in concentration; this supports the general conclusion that plant and animal cells are able to discriminate against radium relative to calcium.

When this observation is taken in conjunction with the previous observation that in animals, at least, the radium distribution in the body is similar to that of calcium, it must be concluded that radium may be taken up and metabolised in the same way as calcium; but there is a discrimination mechanism for excluding radium which operates with an efficiency ranging from ~ 50 to 98%.

Although it is beyond the scope of this chapter to inquire into the physiology of mineral uptake, three distinct physico-chemical mechanisms should be mentioned: adsorption (a surface process); absorption (a metabolically controlled process); and association (a structural factor). Havlik (1971) found that 5 out of 7 species of unicellular algae accumulated more radium by adsorption than by absorption. The reason for this is probably two-fold: unicellular algae have a high surface area-to-volume ratio, and radium has a strong adsorption capacity (chapter 5, this volume). Absorption is the dominant process in higher organisms where the surface area-to-volume ratio is smaller and where distribution between organs (e.g. between flesh and bone) becomes important. Radium uptake by association can occur where contaminated material is associated with a food item without being a direct part of it. For example, submerged aquatic macrophytes accumulate sediment on their structural surfaces, hence radium in this sediment may become part of a herbivore diet simply by association; likewise, animals with digestive systems carry undigested material in their gut at any given time, and even though the radium may be discriminated against in the digestive process, it still becomes part of the diet of any predator which feeds on the whole animal.

The interaction of uptake mechanisms is illustrated in Section 6.6 where the effect of major ions is examined.

6.3. CONCENTRATION FACTORS

Most of the available data on the biological uptake of radium consist of field survey results on radium concentration on diet items (Q) and in the supporting water or sediment (C). All that can generally be calculated from such data is the concentration factor (F):

$$F = Q/C \qquad (6.1)$$

and the variation of Q with C. It is frequently assumed (e.g. ICRP 1979, USNRC 1980) that there is a linear relationship between Q and C (i.e.

F is independent of C). In the following sections this class of data is assembled in log Q v. log C plots and the linearity is tested by comparing the slope of the line against unity using the standard error of regression.

It frequently happens that an organism takes up radium from either or both of two sources; for example, fish are exposed via water and food, and aquatic macrophytes are exposed via water and sediment. If the concentration factors are independent of the concentrations in both sources, then

$$Q = a_1C_1 + a_2C_2 \qquad (6.2)$$

The two concentration factors a_1 and a_2 can be estimated from a multiple regression of Q on C_1 and C_2, constrained through the origin. An important application of this model is to irrigation; Myttenaere et al. (1969) showed that transfer of cesium and cobalt to rice from irrigation water was 10-100 times greater than from soil, but there is insufficient data on radium to describe its transfer during irrigation (Williams 1981).

In the following section, the goodness of fit of the regressions is estimated by the coefficient of determination r^2, expressed as a percentage; this indicates the percentage of the variance that is accounted for by the regression. The statistical significance of the regression is taken from the square root of the coefficient of determination, which is the correlation coefficient r, using tabulated values calculated on the basis of the sample size; the significance is shown as a p value, being the probability that the r value occured by chance.

6.3.1. Algae

The data in Figure 6.1 cover a very wide concentration range (7 orders of magnitude) and give a very good fit to the regression:

$$Q = 441\ C^{1.02} \qquad (6.3)$$

With $r^2 = 94\%$ ($p << 0.001$). The values above 3 x 10^2Bq L^{-1} in water are all taken from laboratory experiments at equilibrium (7-14 days of exposure). The value of the regression coefficient (b = 1.02) is not significantly different from 1, so it can be concluded that uptake of radium from water by algae (including blue-green, unicellular and macroalgae) is a linear process. The equivalent linear regression is

$$Q_a = 432\ C \qquad (6.4)$$

and the concentration factor

$$F = Q/C = 432 \qquad (6.5)$$

6.3.2. Aquatic Vascular Plants

Aquatic vascular plants (macrophytes) may take up radium from water (w) via foliage and from sediment (s) via roots. Figure 6.2 illustrates the relationship between foliage and sediment. The regression is:

$$Q = 0.39\ C_s^{\ 0.49} \qquad (6.6)$$

with $r^2 = 22\%$ and $p < 0.001$. The slope of the regression coefficient, $b = 0.49$, is also significantly different from 1 with p 0.001. The relationship between foliage and water is shown in figure 6.3, where the regression is:

$$Q = 81\ C_w^{\ 1.21} \qquad (6.7)$$

with $r^2 = 50\%$ and $p < 0.001$. The regression coefficient, $b = 1.21$, is not significantly different from 1 and the corresponding linear equation is:

$$Q = 55\ C_w\ . \qquad (6.8)$$

The two-source model (equation 6.2) can also be fitted to these data. The regression is:

$$Q = 8.56\ C_w + 0.014\ C_s \qquad (6.9)$$

for which $r^2 = 51\%$ and $p = 0.01$ for a_1 and $p = 0.02$ for a_2 ($N = 37$). This model is linear, of course, and does not take into account the non-linearity suggested by the plant-sediment relationship in Figure 6.2. It accounts for no more of the variance than the plant-water regression, so it is of questionable value; however, because several different data sets have been pooled, the large variance works against a detailed analysis. In future studies with macrophytes, a further examination should be made of the contribution of the two sources. As it stands this model suggests that at an average water concentration of 0.21 Bq L^{-1} and average sediment concentration of 94 Bq kg^{-1}, 58% of the radium comes from water and 42% comes from sediment.

It is well known that total sediment concentration of an element (C_s) is not a good index of the amount actually available to plant roots, so the non-linearity noted above may be due to the physical and chemical differences between the natural and effluent streams from which the data are taken. From this point of view a systematic study of sediments has been initiated by the Czechoslovak group and a theoretical model has been proposed by van Dorp et al. (1979) which may be useful in interpreting the results.

6.3.3. Insects

The data in Figure 6.4 are all from field surveys and give a good fit to the regression:

$$Q = 186\ C^{0.91} \qquad (6.10)$$

with $r^2 = 81.2\%$ and $P << 0.001$. The regression coefficient $b = 0.91$ is not significantly different from 1 and the corresponding linear regression model is

$$Q = 247\ C \qquad (6.11)$$

for which the concentration factor is 247. Thus it can be assumed that in the region of 10^{-2} to 10^{0} Bq L^{-1}, the uptake process for insects in water is linear.

6.3.4. Fish

The data in Figure 6.5 are all from field surveys and/or field experiments, and give a good fit to the regression

$$Q = 13\ C^{0.68} \qquad (6.12)$$

with $r^2 = 54.5\%$ and $p << 0.001$. The regression coefficient $b = 0.68$ is significantly different from 1 ($p < 0.001$), so the concentration factor will be

$$F = Q/C = 13\ C^{-0.32} \qquad (6.13)$$

This function varies from 119 at 0.001 Bq L^{-1} to 13 at 1 Bq L^{-1}, so it is highly non-linear.

Fish vary widely in their diets and behaviour and some of the individual data sets that are pooled in Figure 6.5 have significantly different intercepts and/or slopes; however pooling is justified on the grounds that it produces a significant general trend, and that the variation in some data sets spans the whole range (e.g. Davy and Conway 1974, Davy and O'Brien 1975).

6.3.5. Mussels

Freshwater mussels (Velesumio angasi) are a significant dietary item for the Aboriginal people in the Arnhem Land region of Northern Australia, where uranium mining is being developed on a large scale (Fox et al. 1977). The available field data for this single species are presented in Figure 6.6. The best-fit regression is

$$Q = 203\ C^{0.78} \qquad (6.14)$$

with $r^2 = 39.2\%$ and $p < 0.001$. The regression coefficient $b = 0.78$ is not significantly different from 1 and the equivalent linear model is

$$Q = 347\ C \qquad (6.15)$$

These mussels are apparently second only to algae in their ability to accumulate radium.

6.4. VARIATION IN CONCENTRATION FACTORS

For the human dietary items, fish and mussel flesh (Figures 6.5, 6.6), the data are scattered either side of the regression lines by a factor of ± 10. This level of uncertainty suggests that the average values for the concentration factor are of little use in dose assessment without the availability of site specific data that may reduce the variance. In the case of fish, the variance may possibly be explained by the variety of fish diets, feeding habits and migration patterns; however in the freshwater mussels, the data (Figure 6.6) refer to a single species in a single region and thus constitute site and species specific data. The cause of this extraordinary variation is being investigated (Jeffree, Australia).

In contrast to the fish and mussel variation, the algal data are remarkably uniform (Figure 6.1). Although they spread within a range of a factor of ± 3 of the regression line, the data represent many different species and habitats, including laboratory culture. It may well be that site and species specific data are much less variable. The insect and macrophyte data (Figures 6.2, 6.3, 6.4) fall between these extremes of variation.

In the following section, it is shown that algae equilibrate very rapidly with radium in water (1-3 days) but fish and mussels have much longer equilibration times; it is therefore suggested that algae be investigated as a monitoring medium, because of their rapid linear and predictable response to variations in the water concentration.

Another source of error in concentration factors calculated from the data assembled here is the difference between the linear and non-linear models. McDowell-Boyer et al. (1980) assumed linearity and calculated concentration factors from the arithmetic mean of the available data on ^{226}Ra in the terrestrial food-chain; however Williams (1981) showed that by using this approach overestimation by a factor of 3 and underestimation by a factor of 30 were possible within the existing aquatic and terrestrial data on radium.

6.5. TIME BEHAVIOUR OF RADIUM UPTAKE

6.5.1. Models for Radium Uptake

When data are available on radium uptake or excretion with time, somewhat more information can be gathered about the process. The simplest theoretical model that can be applied is that of a single compartment subject to linear uptake and loss processes (e.g. ICRP 1959, Hiyama and Shimizu 1969:

$$\frac{dQ}{dt} = uC - \lambda Q \qquad (6.16)$$

Where u is the uptake rate coefficient and λ is the loss rate coefficient. The solution to this equation, assuming that $Q = 0$ when $t = 0$, is

$$Q = \frac{u}{\lambda} C (1-e^{-\lambda t}) \qquad (6.17)$$

At equilibrium this simplifies to

$$Q = \frac{u}{\lambda} C \qquad (6.18)$$

where $\frac{u}{\lambda}$ equals the concentration factor F.

This model adequately describes the uptake of radium in the alga Scenedesmus obliquus, as shown in Figure 6.7 (in the absence of barium, curve $M = 0$). The biological half-life ($T_{1/2}$) for this process was

$$T_{1/2} = \frac{\ln 2}{\lambda} = 0.64 \text{ days} \qquad (6.19)$$

Havlik (1971) found that algae fall into two groups with regard to radium uptake behaviour; one group responds with a monotonic increase in radium concentration with time, achieving equilibrium in about 3 days; the other group shows a maximum uptake after 1 day followed by a decline, lasting about 5 days, to equilibrium. When the adsorbed and absorbed fractions are separated out, in the former species absorption is the dominant process, whereas, in the latter, adsorption is the dominant process. The rapid uptake and subsequent decline in the adsorption dominant process (similar to the response of S. obliquus in the presence of barium, Figure 6.7) can be explained by a rapid surface exchange mechanism which reverses as the radium concentration in water declines as a result of uptake by the algae; the radium concentration in water varied inversely with that in the algae, even in the continuous culture experiments (Havlik and Robertson 1971). A full explanation of radium uptake in algae therefore requires a two-compartment rather than a single-compartment model.

Multi-compartment models are also required in higher organisms, for example in vertebrates in which the skeleton and soft tissues have very different radium retention characteristics. Such models have been used to describe radium uptake and retention in man (ICRP 1973) and in rats (Loevinger et al. 1956), however none have yet been applied to radium uptake in aquatic organisms.

Some data are available on radium retention in fish. Lucas et al. (1979) conducted radium injection experiments on bluegill (Lepomis macrochirus) and, on the basis of results from 2 fish, constructed the following whole-body retention function:

$$R = 0.8\, t^{-0.15} \qquad (6.20)$$

where R is the fraction remaining after 5 days. After 230 days, ~35% of the Ra remained, indicating that equilibrium would be achieved only after a somewhat longer period. As fish are an important dietary item in most cultures, their radium retention characteristics need to be defined more clearly. By comparison, strontium studies in fish have yielded a variety of results; Lucas et al. (1979), quoting other sources, estimated a retention function for the marine grouper which gives 62% retention after 200 days, an Lebedeva (1962) found an experimental equilibrium within

60-120 days in yearling carp. Obviously fish need to be studied for periods of more than a year.

For a simple, linear, one-compartment model, uptake and loss rates of radium can be calculated from the equilibrium time and the concentration factor by using equation (6.19) and assuming that the half-life is about a fifth of the equilibrium time (5 half-lives yield 97% equilibrium in equation 6.17). For example, the 3-day equilibrium in algae yields a half-life of 0.6 days and thus a loss rate of

$$\lambda = \frac{\ln 2}{0.6} = 1.16 \text{ day}^{-1} \qquad (6.21)$$

$$\text{since} \quad F = \frac{u}{\lambda} = 432 \text{ (from Figure 6.1)}$$

$$\therefore \quad u = 501 \text{ day}^{-1}$$

For aquatic macrophytes, Iskra et al. (1970) found an equilibrium time of 12-15 days. A similar equilibrium period (4-12 days) was found by El-Shinawy and Abdel-Malik (1980) for the uptake of phosphorus (a major nutrient), cobalt (a trace nutrient) and cesium (a trace non-nutrient) in 3 aquatic vascular plants, so a common rate of uptake is suggested. From Equation (6.21), an equilibrium time of 12 days yields a biological half-life of 2.4 days, hence a loss rate coefficient of 0.29 days^{-1}, and with a concentration factor of 55 (Figure 6.3) gives an uptake rate coefficient of 16 day^{-1}. This means that algae take up radium about 30 times more rapidly than macrophytes, and lose it 4 times more rapidly, which explains the difference of the factor of 7 between their concentration factors.

6.5.2. Equilibrium Times and Food-Chain Transfer

Radium uptake by organisms that belong to the human food-chain is a dynamic process, and equilibrium is not necessarily achieved at each trophic level (Williams 1981). The degree of equilibrium that is achieved can be assessed by comparing the equilibrium time with the food-chain transfer time. The food-chain transfer time is the interval between the initiation of radium uptake and ingestion by the next link in the food chain.

Algae have the shortest equilibrium time (~ 3 days) and, as this is commensurate with their growth rate, equilibrium can normally be assumed. For macrophytes with their ~ 12 day equilibrium time, equilibrium can be assumed for mature foliage, but for animals which graze exclusively on young growing tissue, equilibrium would not be established.

No data are available on the rate of radium uptake in insects.

For freshwater mussels, Jeffree (Australia) has observed that the radium concentration in flesh continues to increase with age (size) in edible mature animals from a single location, which indicates that equilibrium is not achieved in the harvestable lifetime of the animal; 28-day experiments in which radium uptake was induced also failed to reach equilibrium.

For fish, the Lucas et al. (1979) data analysed previously suggest that radium may be accumulated throughout much of the range of the food-chain transfer time (2-6 years); however this result needs further experimental confirmation.

6.6. MAJOR ION EFFECTS

Uranium mill effluent usually contains high concentrations of dissolved Ca, Mg, SO_4, Mn and/or Cl and thus will change the salinity of the receiving freshwater as well as the radium concentration. The presence or absence of major ions in solution has a strong influence on the biological uptake of non-nutrient trace substances (Polikarpov 1966) and so this effect needs to be quantified for radium uptake.

In a study of four Italian lakes, de Bortoli and Gaglione (1972) found that the calcium concentration (M, mg L^{-1}) influenced the radium concentration factor in fish (F) as follows:

$$F = 460 - 11.83\ M \qquad (6.22)$$

A similar effect on strontium was also observed with the following equation:

$$F = 347 - 7.33\ M \qquad (6.23)$$

For radium, this implies that, if the linear model is correct, the presence of 10 mg L^{-1} of Ca would reduce radium uptake by 26%, and a concentration of ~ 40 mg L^{-1} Ca would suppress accumulation altogether. In agreement with this type of result, Jeffree (Australia) found that uptake of radium by the freshwater mussel Velesunio angasi was suppressed in the presence of 5 mg L^{-1} Ca, but not in the presence of 0.5 mg L^{-1} Ca.

More detailed data were obtained by Sebesta et al. (Czechoslovakia) during experiments on the effect of barium concentration on radium uptake in three species of unicellular algae. Figure 6.7 shows the results for Scenedesmus obliquus in the presence of 0, 0.1, 1.0 and 10 mg L^{-1} of Ba. The data have been normalized to a concentration factor of 440 (from Figure 6.1) since the original data were presented as percentages. The radium concentration in the medium at the beginning of the static experiment was 4000 Bq L^{-1}, and the results shown are the means of repeated experiments.

Equation 6.17 was fitted to the "no barium" data, with $u / \lambda = 440$, $C = 1$ and $\lambda = 1.09$ day^{1}, and $r^2 = 96\%$ for the fit; the half-time of this uptake process is ~ 15 hours. The effect of barium was estimated by fitting a linear regression to the (log) equilibrium concentrations for each of the 3 non-zero treatments (for which $r^2 = 99\%$) and substituting this regression for u/λ in equation (6.17) to give

$$Q = (43 - 33.5 \log M)\ (1 - e^{-1.09t}) \qquad (6.24)$$

This model was then used to predict the uptake behaviour of the barium treatments. As the Figure 6.7 shows, the equilibrium concentrations are well predicted by the model (from 3 days onwards); however, the behaviour at 6 hours was greatly underestimated in all treatments. Havlik (1971) and Havlic and Robertson (1971) found that in some algae rapid adsorption occurred (within 1 day), but absorption did not become significant until after 3 days. The result indicated in Figure 6.7 could therefore be explained if the presence of barium has a greater suppressive effect on radium absorption than it has on radium adsorption.

Several factors may cause the suppression of radium uptake by calcium and barium. Calcium is essential for both the structure and function of membranes, therefore variation in calcium concentration will induce both a Ca-membrane interaction and a Ca-Ra interaction. Active solute uptake through membranes is thought to occur at specific locations where a specialized protein structure acts as a gate (Klingenberg 1981). Kyte (1981) claims that there are only 3 basic "pumps" or types of uptake mechanism: Na^+- K^+, Ca^{++}, and H^+- K^+. It is therefore likely that Ra and other alkaline-earth elements are taken up via the Ca gate.

The simplest Ca-Ra interaction would be that of isotopic dilution, Ra being taken up as if it were Ca. However, this predicts an observed ratio of 1 and thus fails to explain discrimination against Ra relative to Ca (Section 6.2); it also fails to explain why there is an absolute decrease in the amount of radium uptake when there is an increase in calcium uptake. This latter phenomenon might be explained if it could be shown that the discriminatory power of the membrane increased as the Ca concentration increased; this behaviour has been observed in plants (Epstein 1972).

Figure 6.7 shows that increased Ba also suppresses Ra uptake in Algae. This cannot be explained by a Ca-membrane interaction as it is not likely that Ba (a non-nutrient) could make up for a Ca deficiency. Another explanation of the Ba effect can be derived from the fact that the protein gate structures in the cell membrane operate at a finite rate, and hence become saturated as the ion concentration increases. This saturation behaviour has been widely observed and, in the case of plants, was first described theoretically by the Michaelis-Menten enzyme-kinetic equation (Epstein 1972):

$$V = V_m C/(C+K) \qquad (6.25)$$

where V is the rate of uptake, V_m is the maximum rate of uptake and K is the Michaelis constant, equal to the value of C at $V_m/2$. If V is substituted for uC in equation (6.16), then at equilibrium the concentration factor for Ca (and presumably for other solutes taken up via the Ca^{++} gate) will be

$$F = \frac{V}{\lambda C} \qquad (6.26)$$

This equation predicts that when the concentration is low (C K), V will increase in proportion to C and the value of F will remain constant as C increases; however, as the uptake system saturates and C continues to increase (C> K), F will decrease in proportion to 1/C. The increasing dilution of Ra among those elements passing the Ca^{++} gate will therefore cause its uptake to decrease as C increases beyond the saturation point. Presumably Ba could saturate the mechanism and thus reduce Ra uptake just as well as Ca.

In summary, it is clear that Ca and Ba, at least, have a major influence on Ra uptake, and the concentration factor for radium is not independent of the concentration of these elements. Other elements that may also influence Ra uptake are at present unknown.

6.7. BIOLOGICAL TRANSPORT

So far, the discussion has assumed a geographical equilibrium in the distribution of effluent radium, but this is not necessarily a realistic assumption. Effluent streams move with hydrological, chemical and erosion processes, and there is also a biological transport contribution. Two of these biological transport processes are now considered : animal migration and macrophyte - sediment interactions.

6.7.1. Animal Migration

Animal migration has been largely neglected in studies of radium contamination of waterways so there are few site studies that have included relevant information.

In northern Australia, a significant commercial and game fishery is based on barramundi (Lates calcarifer), a migratory species which spends much of its life in freshwaters receiving drainage from uranium mining developments (Pollard 1974). The adults live in the freshwater reaches of the coastal rivers and in their associated streams and waterholes; they migrate down-stream at the beginning of the wet season (December) to spawn in the tidal waters of the estuary. After the eggs hatch and the juveniles develop in the estuary for 1-2 years, they migrate upstream at the end of the wet season (April). As these times of migration are also the best times for catching barramundi, animals from contaminated waters may be taken 50-100 kilometres away from the pollution site. When caught in the estuary, fish which normally live in a polluted, upsteam area could therefore carry a significant percentage of the radium burden of fish caught further upstream, at the site of maximum contamination.

In contrast, another migratory fish of northern Australia is the tarpon, or ox-eye herring (Megalops cyprinoides). It inhabits estuaries but moves into freshwater in summer (wet season) to spawn (Pollard 1974). Fingerlings are often found in freshwater creeks at the end of the wet season but larger juveniles are found back in the estuaries. The exposure that the tarpon might encounter as a fingerling in contaminated freshwater is therefore likely to be minimal since its major growth period is spent elsewhere.

Another example of radium transfer via animal movement is the Asian water buffalo (Bubalis bubalis) which inhabits the freshwater wetlands of Northern Australia; although it is a territorial species (Tulloch 1978), its grazing and camping areas can be several kilometres apart. The meat is used for human consumption, so the feeding habits of family groups need to be monitored. Also the animals defecate, primarily around the campsite, and thus contaminated faeces may lead to a local accumulation of radium in soil. Bird colonies were suggested by Klechkovskii et al. (1973) as a similar source of local accumulation of radionuclides in droppings.

6.7.2. Macrophyte - Sediment Interactions

Radium is very rapidly adsorbed onto sediment in surface waters (see Chapter 5, this volume). Concentrations of up to 35 kBq kg^{-1}Ra-226 in polluted sediments have been reported (Iyengar et al. India, 1978 progress report), however the highest contaminated sediment concentration for which we have corresponding plant data is that of Havlik et al. (1980) where the average concentration is ~ 500 Bq kg^{-1} (Figure 6.2). The macrophyte radium concentration under these conditions was 8 Bq kg^{-1}. If an annual macrophyte production of 10 kg m^{-2} is assumed (Likens 1975) which is dispersed in a 1 metre deep water column, it would amount to 0.08 Bq L^{-1} in the water, which is about 3 times background; by comparison, sediment containing 500 Bq kg^{-1} is contaminated to ~ 40 times background.

It is not possible at this stage to asses the significance of this type of vegetative recycling but it is an effect worthy of further study; it has been identified by Carignan and Kalff (1980) as a nutrient recycling mechanism. Radium transfer in the opposite direction may also be possible, when the water only is contaminated. Mortimer and Kudo (1974) found a doubling of mercury content in sediment supporting Elodea in contaminated water, compared with plant-free sediment, and this may also be possible with radium.

Other possible interactions between vegetation and sediment include the uptake of radium by vegetation, thus making it unavailable for adsorption on sediment; free-floating phytoplankton transporting the radium downstream at a faster rate than it can be adsorbed on sediment; and rooted macrophytes temporarily immobilizing the radium until the foliage begins to decay, thus enabling radium to enter the detritus pools which hydrologically is generally more mobile than mineral sediment. The extent of organic complexation of radium in natural waters is unknown but metal-organic complexes are usually more soluble (Lasheen 1974) and biologically more available (George and Coombs 1977) than surface-adsorbed metals, so it is possible that the radium, after decay of the plant material, is also chemically more mobile than that adsorbed onto sediments.

6.8. SUMMARY AND RECOMMENDATIONS

For animals, at least, it appears that radium is taken up and metabolized in the same way as calcium, however, there seems to be a mechanism in all cells for excluding radium, with an efficiency of 50-98%. There is some evidence that radium behaves differently to calcium in plants. Radium concentration generally decreases with trophic level in the human food-chain.

Algae have a remarkable uptake response to radium; the response is linear over 7 orders of magnitude, rapidly establishes equilibrium and is highly predictable, with 94% of the variance being explained by the linear model. Insects, fish, mussels and macrophytes all have a more variable response.

Throughout the world fish are of key importance in human diet, but show a nonlinear and non-equilibrium radium uptake response, it therefore seems unwise to use a generic model for fish. As an example of locally important dietary item, freshwater mussels also have a greatly variable and non-equilibrium uptake response. Fish, mussels and algae have a reduced radium uptake in the presence of excess Ca or Ba; this effect should not be ignored in fresh waters contaminated by uranium mill waste containing high levels of alkalith elements. The relative contribution of water and diet to radium uptake by any aquatic organism has not been studied.

Animal migration is not a significant factor in mass transport of radium, except for local concentration in faeces produced by colonial animals. Radium may possibly be retained in fish for long periods; this could be significant if a large proportion of seasonal catch has migrated from a polluted area.

There are several ways in which plants interact with sediment; radium incorporated in phytoplankton and/or macrophyte detritus may be transported more rapidly than that incorporated in mineral sediment; radium absorbed from water by macrophyte foliage may be accumulated in sediment more rapidly than in the absence of macrophytes.

It is recommended that future research on the biological uptake and transport of radium be as follows:

a. Obtain site-specific experimental data on radium uptake in fish and other human dietary items (e.g. mussels) with special emphasis on the rate of uptake, the relative contributions of food and water, and the effects of increased Ca, Mg, SO_4 and/or Ba concentrations (the latter when $Ba(Ra)SO_4$ is used in waste water treatment plants).
b. Conduct field and laboratory studies on radium uptake in invertebrates that are significant in fish diets.
c. Evaluate algae as a monitoring medium for radium in fresh waters.
d. Investigate macrophyte-sediment-water interactions to quantify the relative importance of the possible flow directions taking into account seasonal and life-cycle variations and the availability of radium in sediment and water.
e. Conduct comparative studies on plants using radium and calcium and a variety of other nutrient and non-nutrient elements to identify the factors affecting radium uptake and translocation in plants.
f. More thoroughly investigate radium uptake by crops from irrigation water.

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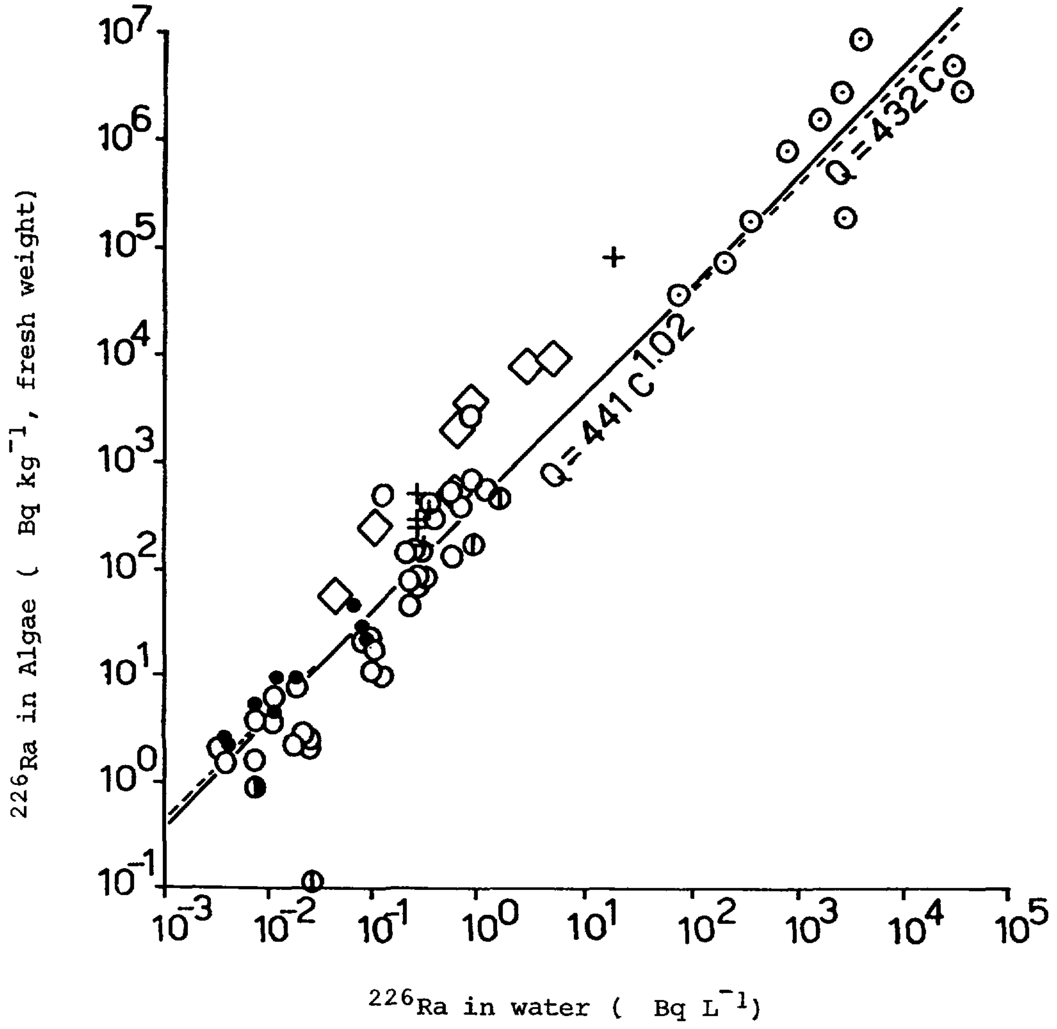

Figure 6.1 The relationship between radium concentration in algae and in the supporting water. ○ = Anderson *et al.* 1963, ● = Martin *et al.* 1969, + = Justyn *et al.* 1979, ⦶ = Markose *et al.* 1980, ◑ = de Jesus, S. Africa, ◇ = Iyengar *et al.* 1980, ○ = Havlik 1971 and Havlik and Robertson 1971 (experimental data). For the regression, $N = 71$, $\bar{X} = -0.409$, $\bar{Y} = 2.226$, $S_b = 0.030$, $r = 0.971$, $p \ll 0.001$. The dotted line represents the linear function. Weight conversions were based on 10% dry matter and 2% ash content.

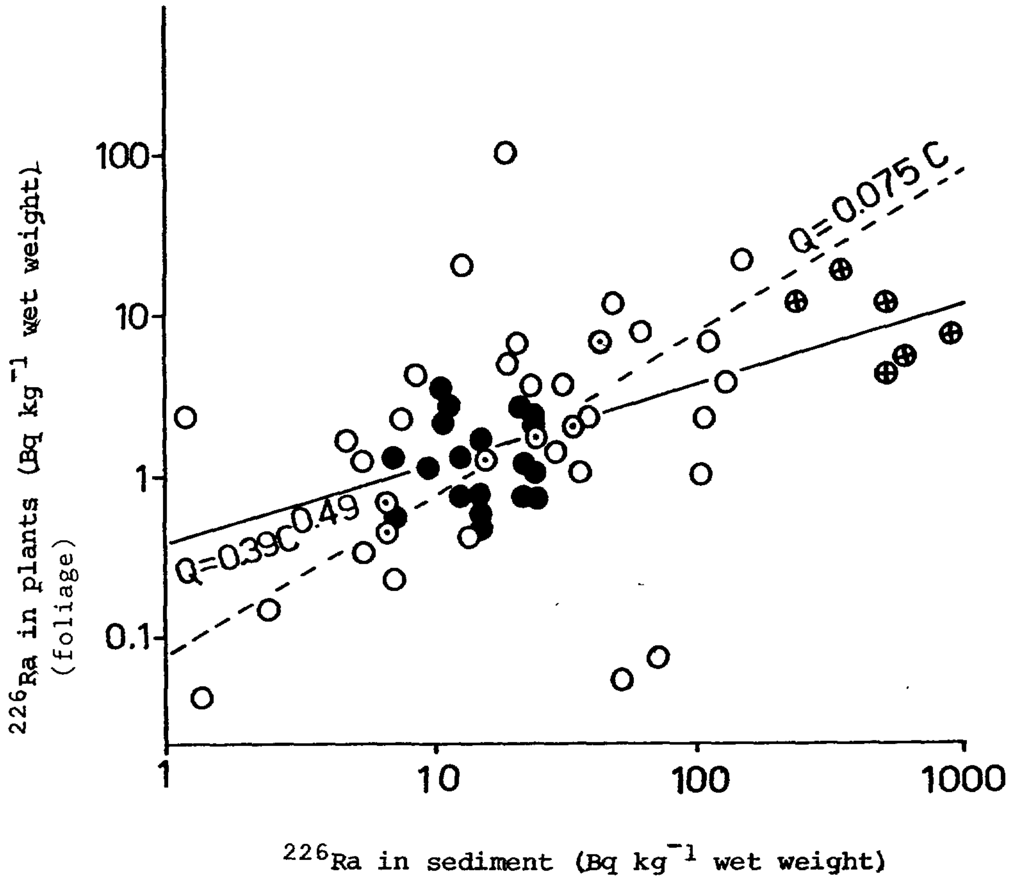

Figure 6.2 Relationship between radium concentration in aquatic macrophytes and in supporting sediment. For the regression, $N = 59$, $\bar{X} = 1.387$, $\bar{Y} = 0.264$, $S_b = 0.121$, $r = 0.472$, $p < 0.001$. The dotted line represents the linear function. Sediment assumed to contain 40% dry matter and 30% ash, plants assumed to contain 10% dry matter, 2% ash. ○ = Havlik 1967, ⊙ = Havlik 1970, ⊕ = Havlik *et al.* 1980, ● = Williams, Australia.

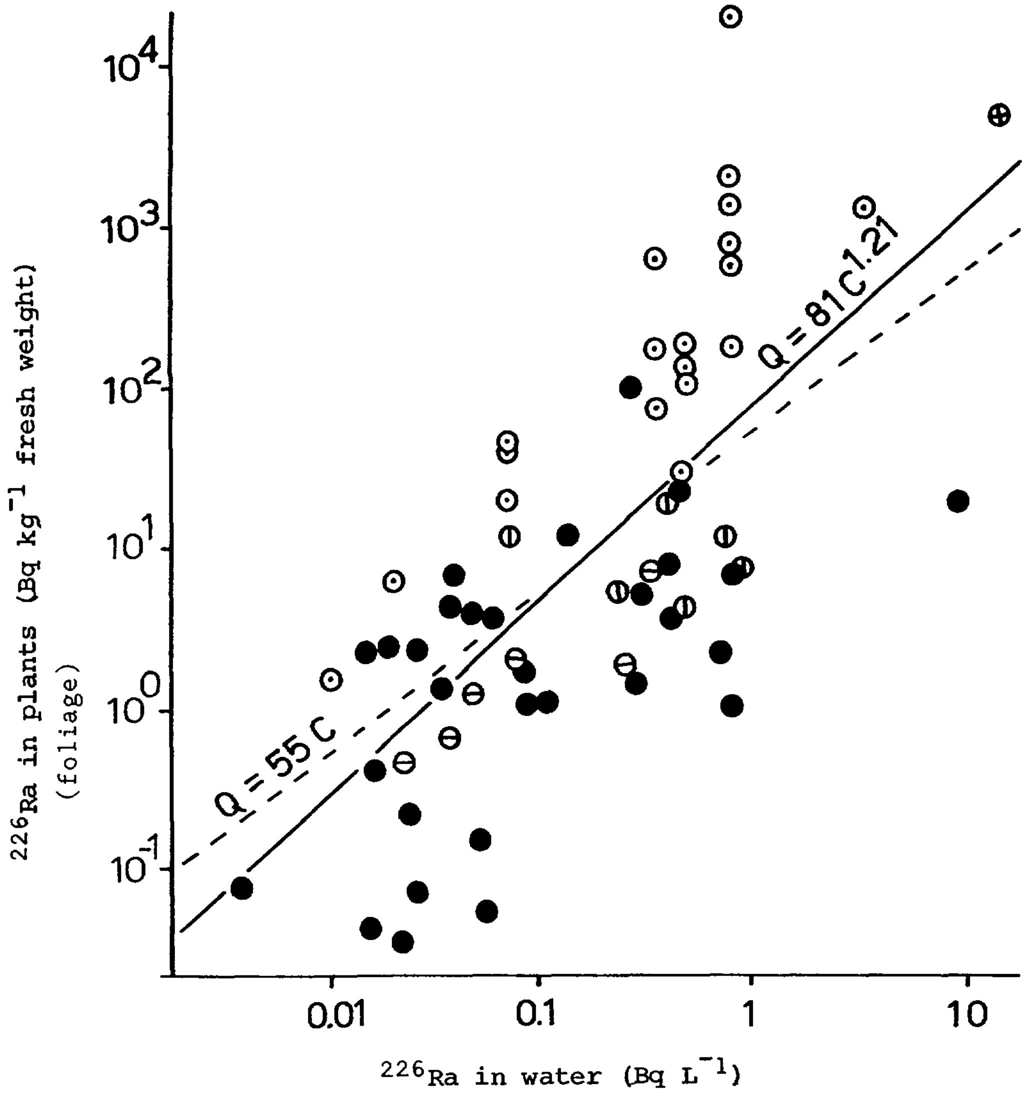

Figure 6.3 Relationship between radium concentration in aquatic macrophytes and in supporting water. For the regression, $N = 62$, $\bar{X} = -0.797$, $\bar{Y} = 0.941$, $S_b = 0.158$, $r = 0.705$, $p < 0.001$. The dashed line represents the linear function. Plants assumed to contain 10% dry matter and 2% ash. ● = Havlik 1967, ⊖ = Havlik 1970, ⦶ = Havlik *et al.* 1980, ⊕ = Pradel, France, ⊙ = Justyn *et al.* 1979.

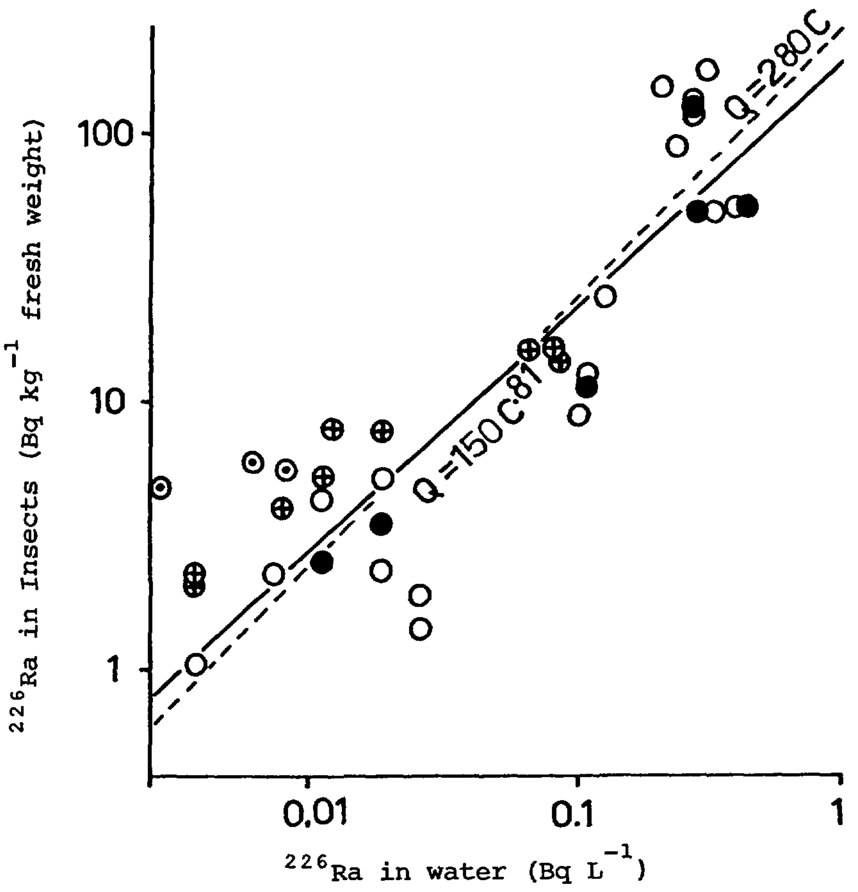

Figure 6.4 Relationship between radium in aquatic insects and in the surrounding water. ○ = Anderson *et al.* 1963, ⊕ = Martin *et al.* 1969, ● = Tsivoglou *et al.* 1960, ⊙ = Stegnar and Kobal 1980, 1981. For the regression $N = 35$, $\bar{X} = 1.395$, $Y = 1.054$, $S_b = 0.079$, $r = 0.873$, $p < 0.001$. The dotted line represents the linear function. Weight conversions were based on 2% ash and 10% dry weight.

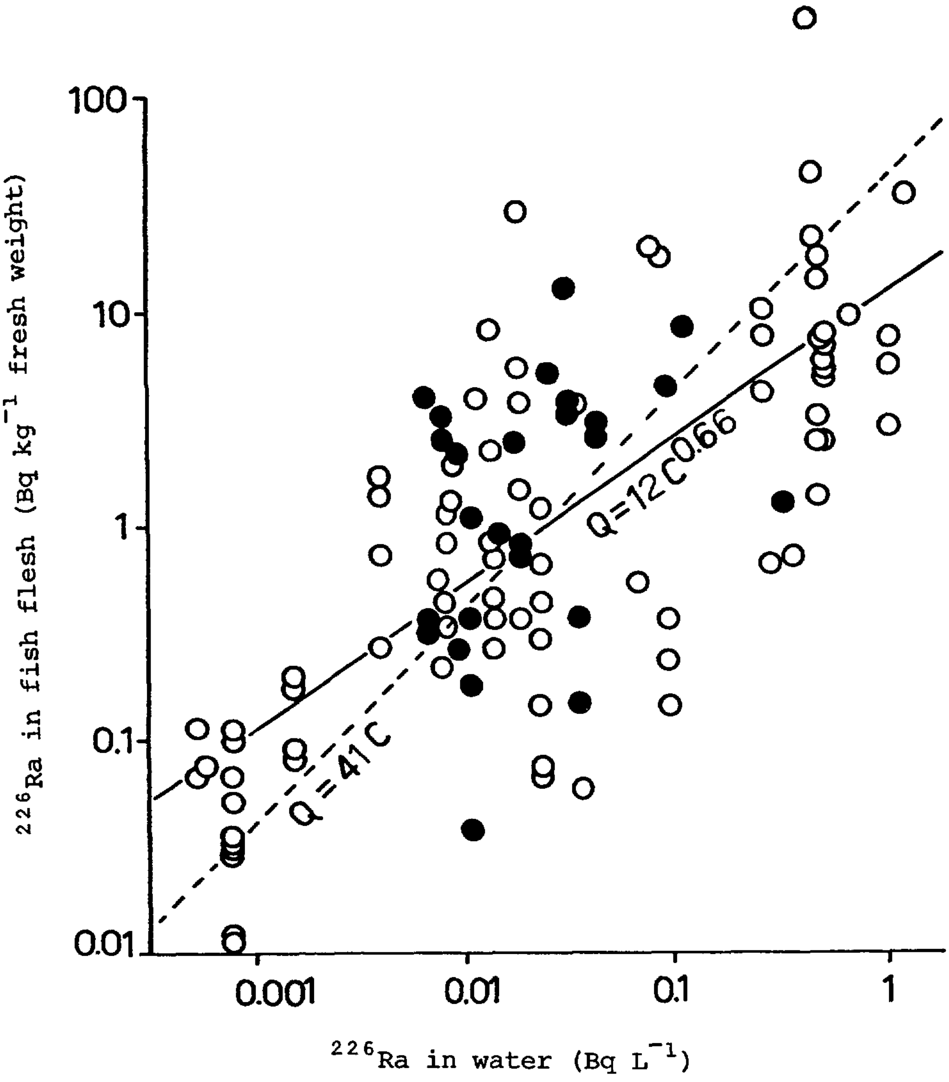

Figure 6.5 Relationship between radium concentration in fish flesh and in the surrounding water. ○ = Anderson *et al.* 1963, Martin *et al.* 1969, de Bortoli and Gaglione 1972, Ettenhuber *et al.* 1975, Justyn *et al.* 1979, Paul *et al.* 1980, Markose *et al.* 1980, Iyengar *et al.* 1980, Iyengar-India, Pradel-France, Stegnar and Kobal 1981, Fourcade *et al.* 1981; ● = Davy and Conway 1974, Davy and O'Brien 1975. For the regression, N = 108, $\bar{X}$ = -1.627, $\bar{Y}$ = 0.01, S_b = 0.062, r = 0.719, $p < 0.001$. The dashed line represents the linear function.

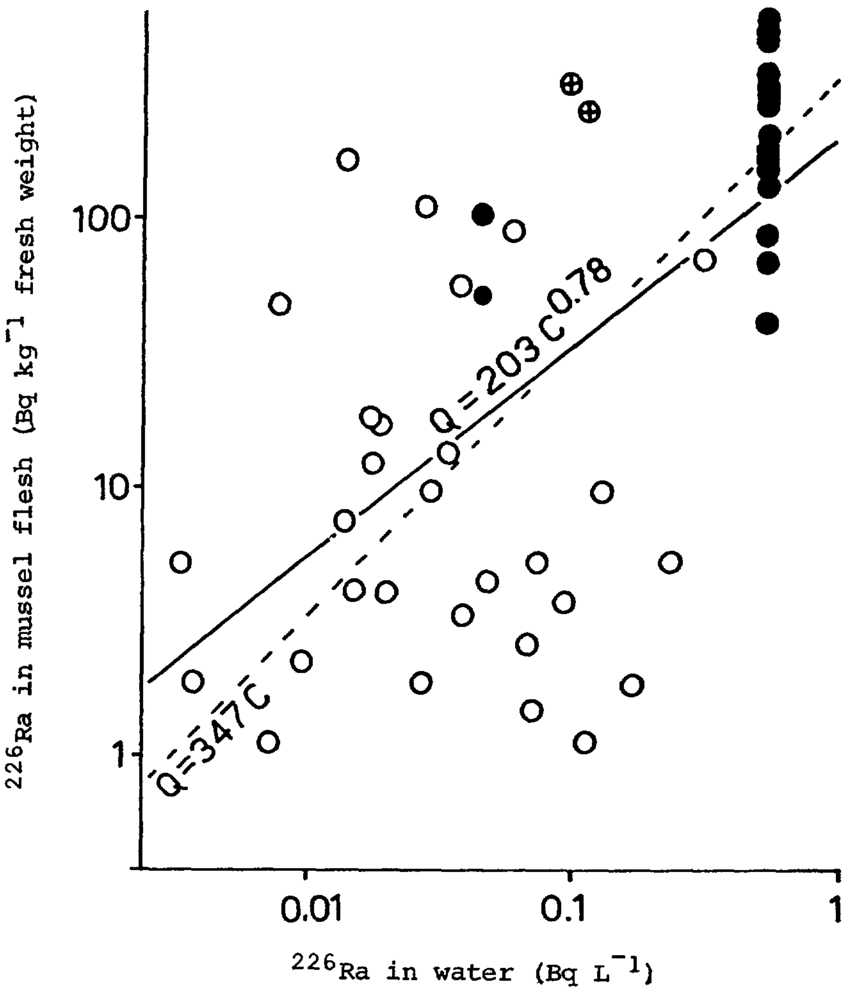

Figure 6.6 Relationship between radium in mussel flesh and in surrounding water.

O = Davy and Conway 1974, ● = Jeffree, Australia,

⊕ = Noranda 1978. For the regression, N = 50,

$\bar{X} = -1.07$, $\bar{Y} = 1.47$, $S_b = 0.140$, $r = 0.626$, $p < 0.001$.

The dotted line represents the linear function.

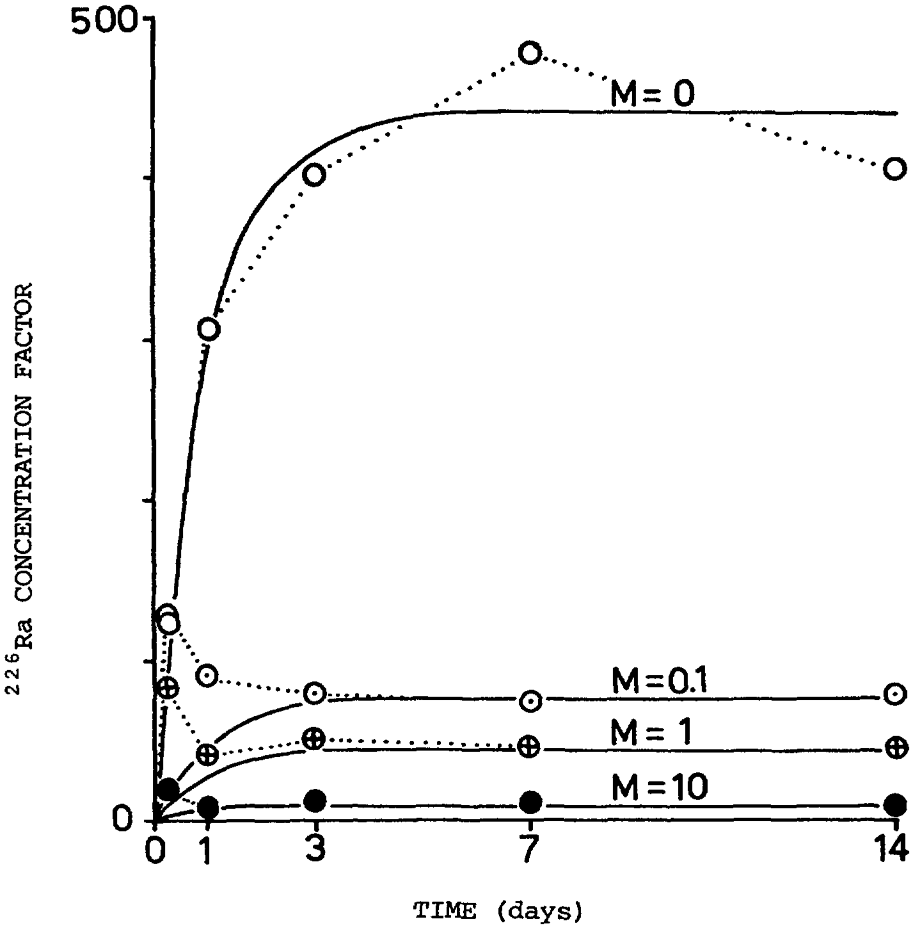

Figure 6.7 The effect of barium concentration (M, mg L^{-1}) on the uptake of radium by *Scenedesmus obliquus*. The solid curves represent the model predictions, the dotted lines join the data points. Data of Sebesta *et al.* (Czechoslovakia).

REFERENCES

ANDERSON J.B., TSIVOGLOU E.C., and SHEARER S.D.,
"Effects of uranium mill wastes on biological fauna of the Animas River (Colorado - New Mexico)".
Radioecology (Proc. First Nat. Symp. on Radioecology, Fort Collins, 1961, ed. V. Schultz and A.W. Klement) Rheinhold and A.I.B.S., Washington (1963) 373-383.

BHUJBAL B.M., D'SOUZA T.J. and MISTRY K.B.,
"Discrimination between radium and calcium in the soil-plant system".
Radiation and Radioisotopes in Soil Studies and Plant Nutrition (Proc. Symp. Bangalore, 1970) FAO and Indian Dept. of Atomic Energy, Bombay (1971) 155-165.

BROWNSCOMBE A.J., DAVY D.R., GILES M.S. and WILLIAMS A.R.,
Three Baseline Studies in the Environment of the Uranium Deposit at Yeelirrie, Western Australia.
Australian Atomic Energy Commission, Lucas Heights, AAEC/E442 (1978).

CARIGNAN R. and KALFF J.,
Phosphorus sources for aquatic weeds: water or sediment?
Science 207 (1980) 987-989.

DAVY D.R. and CONWAY N.F.,
"Environmental studies, Northern Territory uranium province 1971/73".
The Alligator Rivers Area Fact Finding Study - Four AAEC Reports, Australian Atomic Energy Commission, Lucas Heights, AAEC/E305 (1974) III.

DAVY D.R. and O'BRIEN B.G.,
"Radiological aspects".
Rum Jungle Environmental Studies (ed. D.R. Davy), Australian Atomic Energy Commission, Lucas Heights AAEC/E365 (1975) Ch. 9.

DE BORTOLI M. and GAGLIONE P.,
Radium-226 in environmental materials and foods,
Health Physics 22 (1972) 43-48.

EL-SHINAWY R.M.K. and ABDEL-MALIK W.E.Y.,
Retention of radionuclides by some aquatic freshwater plants.
Hydrobiologia 69 (1980) 125-129.

EPSTEIN E.,
Mineral Nutrition of Plants: Principles and Perspectives,
John Wiley, New York (1972) Ch. 6.

ETTENHUBER E., CLAJUS P. and ROEHNSCH W.,
Bestimmung der Akkumulationfactoren Fisch/Wasser einiger fur die Strahlenbelastung des Menschen Wichtiger Radionuklide.
Staatliches Amt Für Atomsicherheit Und Strahlenschutz SAAS-175 (1975).

FOURCADE N., MARPLE M.L. and ZETTWOOG P.,
"Le radium-226 dans la chaine alimentaire au voisinage d'une mine et d'usine de traitement d'uranium situées dans le centre de la France".
Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle (Proc. Int. Symp. Knoxville, 1981) International Atomic Energy Agency, Vienna, IAEA-SM-257 (1981) paper 97P.

FOX R.W., KELLEHER G.G. and KERR C.B.,
Ranger Uranium Environmental Inquiry. Second report, Australia Govt. Publishing Service. Canberra (1977).

GEORGE S.G. and COOMBS T.L.,
The effects of chelating agents on the uptake and accumulation of cadmium by Mytilus edulis.
Marine Biology 39 (1977) 261-268.

HAVLIK B.,
Cumulation of radioactive substances by organisms of natural biocenosis of surface waters and its significance for determination of radioactive load.
J. Hyg. Epidem. Microbiol. Immunol. 11 (1967) 229-245.

HAVLIK B.,
Radioactive pollution of rivers in Czechoslovakia.
Health Physics 19 (1970) 617-624.

HAVLIK B. and ROBERTSON E.,
"Radium uptake by freshwater algae".
Radionuclides in Ecosystems (Proc. IIIrd National Symp. on radioecology, Oak Ridge 1971), CONF-710501-P1 (1971) 372-380.

HAVLIK B., HANUSOVA J. and MARTINEC M.,
Radioactivity of surface water in the Ploucnice River Basin.
Ceskoslovenska Hygiena 25 (1980) 77-83 (In Czech).

HIYAMA Y. and SHIMIZU M.,
"Uptake of radionuclides by aquatic organisms: the application of the exponential model".
Environmental Contamination by Radioactive Materials (Proc. of Seminar, Vienna, 1969) International Atomic Energy Agency, Vienna (1969) 463-476.

ICRP,
Permissible Dose for Internal Radiation.
International Commission on Radiological Protection, Pergamon, Oxford, Publication No. 2 (1959) 16.

ICRP,
Alkaline Earth Metabolism in Adult Man.
International Commission on Radiological Protection, Pergamon, Oxford, Publication No. 20 (1973).

ICRP,
Report of the Task Group on Reference Man.
International Commission on Radiological Protection, Pergamon, Oxford, Publication No. 23 (1975) Ch. 2.

ICRP,
Radionuclide Release in the Environment: Assessment of Doses to Man.
International Commission on Radiological Protection, Publication No. 29, Annals of the ICRP 2, 2(1979) C.

ISKRA A.A., KULIKOV N.V. and BAKHUROV V.G.,
Role of freshwater vegetation in processes of migration and distribution of natural radioactive elements in the reservoir.
Transl. from Ekologiya 2 (1970) 83-89, in Soviet J. Ecology 1 (1970) 157-162.

IYENGAR M.A.R., RAJAN M.P., GANAPATHY S. and KAMATH P.R.,
"Sources of radiation exposure in a low monazite environment".
The Natural Radiation Environment - III (Symp. Proc., Houston, 1978). Technical Information Centre, Springfield, CONF-780422 (1980) 1090-1106.

JUSTYN J., MARVAN P. and ROSOL J.,
Radioactive wastes and aquatic organisms.
Vydal Vyzkumny ustav vodohospodarsky ve Statnim zemedelskem nakladatelstvi, Praha, Prace and Studie Sesit 151 (1979) 43-214 (In Czech).

KIRCHMANN, R., BOULENGER R., LAFONTAINE A.,
"Absorption du ^{226}Ra par les plantes cultivées".
Proc. First Int. Cong. of Radiation Protection (Rome, 1966) Pergamon, Oxford (1968) 1045-1051.

KLECHKOVSHII V.M., POLIKARPOV G.G., ALEKSAKHIN R.M. (Eds),
Radioecology.
(Transl. Ed. D. Greenberg) Wiley, New York (1973) 251.

KLINGENBERG M.,
Membrane protein oligomeric structure and transport function.
Nature 290 (1981) 449-454.

KYTE J.,
Molecular considerations relevant to the mechanism of active transport.
Nature 292 (1981) 201-204.

LASHEEN M.R.M.W.,
Factors influencing metal uptake and release by sediments in aquatic environments.
Ph.D. Thesis, University of Michigan, Ann Arbor (1974).

LEBEDEVA G.D.,
Principal points of entry of strontium-89 into benthos-eating fishes in freshwater.
Radiobiologiya 2 1 (1962) 43-49 (AEC-TR-5428, 62-71).

LIKENS G.D.,
"Primary production of inland aquatic ecosystems"
Primary Productivity of the Biosphere, Ed. H. Leith, R.H. Whittaker, Springer-Verlag, Berlin (1975) Ch. 9.

LOEVINGER R., HOLT J.G., HINE G.J.,
"Internally administered radiosiotopes".
Radiation Dosimetry, Ed. G.J. Hine, G.L. Brownell, Academic Press, New York (1956) Ch. 17.

LUCAS H.F., SIMMONS J., MARKUN F., FARNHAM J. and KEENAN M.,
Radon and radium retention in the bluegill.
Health Physics 36 (1979) 147-152.

MARKOSE P.M., EAPPEN K.P., VENKATARAMAN S. and KAMATH P.R.,
"Distribution of radium and chemical toxins in the environment of a uranium complex".
Natural Radiation Environment III (Proc. Symp. Houston, 1978) Technical Information Centre, Springfield, CONF-780422 (1980) 1655-1667.

MARTIN S.S., HEIM W.T. and SIGLER W.F.,
"Accumulation of ^{226}Ra in two aquatic ecosystems".
Symposium on Radioecology (Proc. 2nd Nat. Symp., Ann Arbor, 1967, D.J. Nelson and F.C. Evans eds.) CONF-670503 (1969) 307-318.

McDOWELL-BOYER L.M., WATSON A.P. and TRAVIS, C.C.,
A review of parameters describing food-chain transport of lead-210 and radium-226.
Nuclear Safety 21 4 (1980) 486.

MORTIMER D.C. and KUDO A.,
"Interaction between aquatic plants and river bed sediments in the uptake of mercury from flowing water".
Proc. Int. Conf. on Transport of Persistent Chemicals in Aquatic Ecosystems (Ottawa, 1974) National Research Council of Canada, Ottawa (1974) III 11-15.

MYTTENAERE C., BOURDEAU P. and BITTEL R.,
"Importance relative de l'eau et du sol dans la contamination indirecte en radiocesium et radiocobalt de rivières irriguées".
Environmental Contamination by Radioactive Materials (Proc. Seminar Vienna, 1969) International Atomic Energy Agency, Vienna (1969) 175-182.

NORANDA, KOONGARRA PROJECT,
Draft Environmental Impact Statement.
Noranda Australia Ltd., Melbourne (1978) Appendix I.

PAUL A.C., LONDHE V.S. and PILLAI K.C.,
"Radium-228 and radium-226 levels in river environment and its modification by human activities".
Natural Radiation Environment III (Proc. Symp. Houston 1978) Technical Information Centre, Springfield, CONF-780422 (1980) 1633-1654.

POLIKARPOV G.C.,
"Regularities of uptake and accumulation of radionuclides in aquatic organisms". Radioecological Concentration Processes (Proc. Int. Sym. Stockholm, 1966) Pergamon, Oxford (1967) 819.

POLLARD D.A.,
"Freshwater fishes of the Alligator Rivers 'Uranium Province' area (Top End, Northern Territory) with particular reference to the Magela Creek Catchment (East Alligator River System)".
The Alligator Rivers Area Fact Finding Study: Four AAEC Reports, Australian Atomic Energy Commission, Lucas Heights, AAEC/E305 (1974) I 1-71.

SMITH K.A.,
The comparative uptake and translocation by plants of calcium, strontium, barium and radium, 1. Bertholletia excelsa (Brazil Nut Tree).
Plant and Soil 34 (1971) 369-379.

SMITH K.A.,
The comparative uptake and translocation by plants of calcium, strontium, barium and radium, II. Triticum vulgare (wheat).
Plant and Soil 34 (1971) 643-651.

STEGNAR P., KOBAL I.,
Radioecology of uranium and radium with special reference to a uranium mining area".
International Studies on the Radioecology of the Danube River 1976-1979, International Atomic Energy Agency IAEA-TECDOC-229 (1980) 175.

STEGNAR P., KOBAL I.,
"Uptake and distribution of radium and uranium in the aquatic food chain".
Migration in the Terrestrial Environment of Long-lived radionuclides from the Nuclear Fuel Cycle (Proc. Int. Symp. Knoxville, 1981). International Atomic Energy Agency, Vienna IAEA-SM-257 (1981) paper 87P.

TSIVOGLOU E.C., STEIN M., and TOWNE W.W.,
Control of radioactive pollution of the Animas River.
J. Water Poll. Control Fed. 32 (1960) 262-287.

TULLOCH D.,
The water buffalo, Bubalis bubalis, in Australia: grouping and home range.
Aust. Wildl. Res. 5 (1978) 327-354.

USNRC,
Final Generic Environmental Impact Statement on Uranium Milling.
U.S. Nuclear Regulatory Commission, Washington, NUREG-0706 (1980) Vol.3.

VAN DORP F., ELEVELD R. and FRISSEL M.J.,
"A new approach for soil-plant transfer calculations".
Biological Implications of Radionuclides Released from Nuclear Industries (Proc. Int. Symp.; Vienna, 1979) International Atomic Energy Agency, Vienna (1979) 399-406.

WILLIAMS A.R.,
"Biological uptake and transfer of ^{226}Ra: a review".
Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle (Proc. Int. Symp. Knoxville, 1981) International Atomic Energy Agency, Vienna IAEA-SM-257 (1981) paper 92.

Chapter 7

DOSE ASSESSMENT

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7.1. BASIC CONCEPTS

The basic concepts associated with radiation protection have been under development for many years now. The doses to total body and to bone from a body burden of ^{226}Ra have an historical interest, since in the development of the basic concepts for radiation protection the body burdens of other radionuclides were compared to that of radium by the Committee II or the International Commission of Radiological Protection (ICRP, 1960).

7.1.1. Absorbed Dose and Dose Equivalent

The internal radiation dose absorbed per Bq(*) deposited in any part of the human body depends upon the decay scheme of the radionuclide, its distribution throughout the body or organ, and the time integral of the radioactive concentration at a time t, which takes into account the residence time of the radionuclide in the human body. In addition to the concept of absorbed dose(**), D, just mentioned, the concept of dose-equivalent(***), H, has also been introduced in the field of radiation protection to improve the correlation between the deleterious effects of exposure to radiation and the absorbed dose.

The conceptual basis for the determination of dose equivalent is discussed in the ICRU Report 25 (1976). An excerpt from this ICRU report is presented below.

"In the case of internal irradiation, estimates are made of the value of the dose equivalent in real, though stylized, human bodies by calculation from one or more of the following three kinds of information:

(i) environmental or dietary information, leading to estimates of the intake of radioactive materials into the body;

(ii) measurements of radiation emitted from the body or activity in body fluids, leading to estimates of activity in the body or parts of the body;

(iii) measurements of the activity of excreta or exhaled air, leading to estimates of the rate of loss of activity from the body and thus of the activity in the body."

(*) 1 Bq (bequerel) = 27 pCi.

(**) The absorbed dose D is defined by the International Commission on Radiation Units and Measurements Report 33 (ICRU, 1980) as: "The quotient of $d\bar{\xi}$ by dm, where $d\bar{\xi}$ is the mean energy imparted by ionizing radiation to matter of mass dm. $D = d\bar{\xi} / dm$", and the special name for the unit for absorbed dose is gray (Gy). [1 Gy = 100 rad].

(***) The dose equivalent H is defined by the ICRU Report 33 (1980) as: "the product of D, Q and N at the point of interest in tissue where D is the absorbed dose, Q is the quality factor, and N is the product of all other modifying factors. $H = DQN$", and the special name for the unit of dose equivalent is sievert (Sv), [1 Sv = 100 rem].

7.1.2. Dosimetric and Dose Assessment Models

The dose equivalent is usually estimated from a dosimetric model. This implies the existence of human metabolic model describing the uptake of a nuclide from ingestion, deposition in various organs, and the resulting radiation dose equivalent to these organs, after discounting the excretion from the body.

The ICRP Publication 29 (1979a) states the following: "The dose limits for individual members of the public apply no matter how many individuals are exposed, but the requirement to keep doses as low as reasonably achievable necessarily involves consideration of the number of people exposed and the dose distribution among them."

As a consequence, a dose assessment model also becomes necessary. This model describe the radionuclide source, the exposure pathways and the population of exposed persons, and should yield an estimate of dose equivalent for a given source strength. In some cases when the basic data are available the exposed biota can also be included in the dose assessment model. Simplified pathways between radioactive materials released to ground or surface waters and human beings can be seen in Figure 1.

Computational dosimetric models to biota are scattered in the literature (Woodhead 1973, 1974, Blaylock and Witherspoon 1975, Le Clare et al. 1975, Preston 1975, IAEA 1976, Till 1978, Paschoa and Baptista 1978, Paschoa et al. 1979b, Templeton 1979, IAEA 1979b, Paschoa et al. 1981a), however, the diversity, specificity and complexity of most of such models make particularly difficult the adoption of a standardized methodology to calculate dose to biota.

The ICRP Publication 29 (1979a) admonished prudently the following: "In almost all situations, the need to limit doses to man to low levels will ensure that doses to other organisms will not be large enough to cause ecological changes. Nevertheless, the possibility should always be reviewed in the preoperational assessments of proposed or expected releases."

The range of environmental dose rates experienced by aquatic biota was shown earlier to be 10^{-7} to 10^{-2} Gy.h^{-1} (IAEA 1979), when was also emphasized that irradiation experiments with aquatic organisms within this range would be most relevant to environmental studies. More recently the range of internal dose rate to plankton from natural and man-made alpha emitters was estimated to be 10^{-6} to 10^{-1} μGy.h^{-1}

(Paschoa et al. 1981a). These authors suggested that since five orders of magnitude are covered by the range of estimated internal alpha dose rates, further research should be undertaken in the direction of the knowledge of the internal distribution of the alpha doses to plankton to distinct species in order to allow realistic predictions of the potential effects on these organisms resulting from routine or accidental releases of alpha emitters from the nuclear fuel cycle.

7.1.3. Dose Assessment Based Upon ICRP Publication 26

The ICRP dose limits are designed to protect individual workers, and by extension, individual members of the public. Thus the first priority in waste release to the environment is to keep the dose to individual members of the public below the specified limits. The concept of collective dose was later introduced by the ICRP Publication 26 (1977b) to provide quantitative information for radiation protection of populations. The practical application of the concepts associated with collective dosimetry to the front end of the nuclear fuel cycle, however, it still very limited, as pointed out by Paschoa et al. (1981b).

As mentioned by Paschoa et al. (1981b), the relatively new concepts introduced by the ICRP Publication 26 (1977b), and promptly adopted as a policy by the IAEA, Safety Series No. 45 (IAEA, 1978), seem to be more difficult to apply to the case of ^{226}Ra dose limits to the front end of the nuclear fuel cycle than anticipated, because time-varying parameters may have to be treated as constants while other parameters may be ignored, and uncertainties associated with extrapolations from inaccurate data may not be taken properly into account in the evaluation of the collective dose equivalent associated with the front end of the nuclear fuel cycle.

7.1.4. The Concept of Collective Dose Equivalent

There are several shortcomings involved in formulating a complex dose assessment model, as the ICRP Publication 26 (1977b) points out clearly; the paragraph 22 defines the concept of collective dose equivalent in a carefully worded statement as follows:
"The relationship between detriment and the distribution of dose equivalent in an exposed population is not simple, and no single quantity can adequately represent the distribution for the purpose of assessing detriment. Nevertheless, there are many situations in which available use can be made of the quantity called collective dose equivalent. The collective dose equivalent (S) in a population is defined by the expression

$$S = \Sigma_i H_i P_i \qquad (1)$$

where H_i is the per caput dose equivalent in the whole body or any specified organ or tissue of the P_i members of sub group (i) of the exposed population."

Paragraph 219 of ICRP Publication 26 acknowledges the difficulties in applying the system of dose limitation to cases such as, for example, the exposure due to dispersion in the environment of radioactive materials, the exposure due to a natural source of radiation or to practices in everyday life that cause an increase in the level of dose resulting from the natural background of radiation; they use the following careful wording:
"Because of its complexity, assessment of collective dose equivalent involve the use of simplifications and approximations, particularly when a large population is irradiated at low dose levels. Because of this, they may involve considerable uncertainties and these must be borne in mind when the assessment are being used to appraise the detriment associated with practice."

7.1.5. Earlier ICRP Concepts

7.1.5.1. Recall on the concept of Maximum Permissible Dose (MPD)

The ICRP has used for a number of years the following concept associated with risk (ICRP 1966c):
"...any exposure to radiation may carry some risks for the development of somatic effects, including leukaemia and other malignancies, and other hereditary effects." Thus, "The probability of radiation damage manifesting itself during the lifetime of an individual varies with the particular tissue or tissues exposed, with the importance of the function of the constituent cells, with the capacity of the impaired cells to replicate, and possibly, with the means of disposal or replacement of damaged cells."

The concept of maximum permissible dose (MPD) was introduced to quantify a degree of risk associated with a limit of radiation dose at which the assumed risk was deemed to be acceptable to the individual and to society in view of the benefits derived from activities involving exposures to ionizing radiation.

These earlier concepts associated with risk are somewhat related to the UNSCEAR reports (1964, 1966) and to the ICRP publications 2, 8 and 9 (1960, 1966 b,c).

The historical reasons behind the ICRP recommendations were examined by Morgan (1973a) who also called the attention to the possibility that the linear model might not be the most conservative one to evaluate risks from ionizing radiation (Morgan 1973b).

7.1.5.2. Calculation of Maximum Permissible Concentrations from MPC - the case of radium

The MPD concept gave rise to the maximum permissible concentrations in air $(MPC)_a$ and in water $(MPC)_w$. Both the $(MPC)_a$ and the $(MPC)_w$ can be calculated based upon either the power function or the exponential model (ICRP 1960). For comparison purposes the ICRP computed the MPC values according to the power function and the exponential model for the radionuclides of Sr, Ra, Pu and U, which have an effective half-life exceeding 20 days. For ^{226}Ra the $(MPC)_c$ calculated by the power function was 1x10^{-6}μCi/cm^3(*), however, the adopted values for radiation protection were 4x10^{-7}μCi/cm^3(**) for soluble ^{226}Ra, selecting bone as the critical organ, and assuming a maximum permissible body burden MPBB of 0.1 μCi (0.1 μg ^{226}Ra or about 3.7 x 10^4 Bq).

(*) 1x10^{-6}μCi/cm^3 = 1x10^{3}pCi/l = 37 Bq/l.

(**) 4x10^{-7}μCi/cm = 400 pCi/l = 15 Bq/l.

The direct comparison between the body burden q of a specific radionuclide and that body burden of ^{226}Ra q^{Ra} was made based upon the energy deposited in bone by ^{226}Ra and the specific radionuclide in question. Thus, the quantity q could be written as follows (ICRP 1960):

$$q = \frac{q^{Ra} \, f_2^{\ Ra}}{f_2} \cdot \frac{\epsilon^{Ra}}{\epsilon} = \frac{11}{f_2 E} \qquad (2)$$

$$\text{with } \epsilon = \Sigma_i \ E_i \quad F(RBE)_i \ n_i$$

where - q^{Ra} (= 0.1 µCi) is the maximum permissible body burden of ^{226}Ra;
- f_2 is the fraction of radionuclide in the skeleton of that in the total body ($f^{Ra} = 0.99$);
- ϵ is the effective absorbed energy per disintegration of a radionuclide (ϵ^{Ra} = 110 MeV);
- E is the energy (MeV) deposited in skeleton per disintegration;
- RBE is the relative biological effectiveness (1 for X, β^-, β^+, e^-, it is set equal to 1.7 if the maximum energy $E_m \geqq 0.03$ MeV for β^-, β^+ or e^-, equal to 10 for α, and 20 for recoil atoms);
- F is the fraction of disintegrations of daughter to disintegrations of parent.

The ICRP (1960) assumed that the total energy deposited in the skeleton per disintegration of ^{226}Ra plus 30 percent of its daughter products is 11 MeV, and thus the effective energy deposited in the skeleton is Σ E F (RBE)n = 110 MeV.
An average absorbed dose rate (see Appendix I, ICRP 1960) to the bone of 0.06 rad/week or a rate of dose equivalent to the bone of 0,56 rem/week was calculated from a body burden of 0.1 µCi/^{226}Ra and its daughter products.

7.1.5.3. Evolution of criteria for evaluation of the Maximum Permissible Body Burden of Radium-226

The ICRP Publication 1 (1960) called the attention to the fact that "although tumors have not been observed in persons with body burdens of radium as low as 0.1 µCi, the factor of safety may not be as large as 10 because tumors have occured in persons having a body burden less than 1 µCi of radium at the time the tumor was first detected." However, the maximum permissible body burden of 0.1 µCi^{226}Ra was then maintained by the ICRP Publication 2 based upon the following reasoning:

(a) radium does not irradiate the entire hematopoietic system;
(b) body burdens of 0.1 µCi of ^{226}Ra probably produce detectable changes in the bone but are not known to have caused serious damage (demonstrable harm to the individual);
(c) the principal recognizable damage from ^{226}Ra is the production of bone tumors, but the lowest body burden that has resulted in a tumor is 0.5 µCi;
(d) all radium-produced tumors have occured in persons whose original body burdens has been much greater than at the time the tumors were discovered;

(e) most bone tumors arising in radium dial painters may be attributed to ^{226}Ra + ^{228}Ra in which the integrated RBE dose was much greater than would be indicated by the ^{226}Ra burden at the time the tumors were discovered; and

(f) the maximum permissible body burden of a bone-seeking radionuclide corresponding to 0.1 μCi of ^{226}Ra is not reached except following continuous exposure at the MPC values."

Thus, the dose limits recommended by the ICRP Publication 2 were based upon the assumption that a body burden of 0.1μCi ^{226}Ra carried "no effect" as far as bone tumors were concerned.

The ICRP Publication 9 (1966c) established that the MPD for occupational exposure should be regarded as upper limits and the annual dose limits for members of the public should be one-tenth of the corresponding annual occupational MPD.

A precise definition for "members of the public" was unfeasible for dosimetric purposes because it would depend on factors such as differences in age, size, metabolism, customs, and environmental variations. Then, the concept of critical groups within the population was introduced, assuming that any such critical group was "small enough to be homogeneous with respect to age, diet and those aspects of behaviour that affect the dose received" (ICRP 1966c). Among the factors which might affect the design of a routine survey for radioactivity outside the boundaries of a nuclear installation should be included the population distribution and habits of the critical group (ICRP 1966a).

7.2. APPLICATION OF COLLECTIVE DOSIMETRY TO URANIUM MINING AND MILLING

Uranium mining and milling is a practice in which exposure may occur due to dispersion in the environment of uranium daughter products, in particular ^{230}Th, ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po. Relevant data for the internal dose estimates to an individual from intake of those radionuclides are published and summarized in the open literature (Wrenn 1977, ICRP 1979b, ICRP 1980). However, the literature presents only very few examples of estimations of collective exposure of populations due to specific uranium mining and/or milling operations.

Ra-226 is considered to be the most significant nuclide in water releases from mining and milling operations (Kristan et al. 1974). Contamination of water an aquatic biota near uranium mining and milling sites has been reported on a number of occasions (Tsivoglou 1963, Havlik et al. 1968a,b, Havlik 1970, Iyengar and Markose 1970b, Kirchmann et al. 1971, Pradel and Zettwoog 1974, Kaufmann et al. 1975, Siek 1977, UNSCEAR 1977, APS 1978, Sebesta et al. Czechoslovakia, Kurokawa and Kurosawa, Japan, de Jesus et al. , South Africa, Marple and Zettwoog, France), and baseline studies prior to the beginning of uranium operations have also been performed (Brownscombe et al. 1978, Paschoa et al. 1979).

Table 7.1 shows simplified estimates of collective dose commitments from mining and milling operations taken from United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR 1977) and American Physical Society (APS, 1978). The estimates presented in Table I are based upon incomplete dose assessment models.

The site of occurence of a uranium deposit economically feasible to be mined depends on geological parameters unbound to any of the criteria used for site selection for location of other facilities of the nuclear fuel cycle. As a consequence, dose assessment models for uranium mining in particular have to be based upon site specific environmental models which may not apply to more than one situation. The impact of milling facilities located near the uranium mining sites may take advantage of the same site specific environmental models developed for uranium mining operations. In any case, an effort to make more realistic estimates of collective dose commitments from mining and milling operations ought to be made if the decision-making processes are to be based upon those estimates.

The ICRP recommendations have been tentatively applied to estimate the ^{226}Ra collective dosimetry for surface waters in the uranium mining region of Poços de Caldas (Paschoa et al. 1980), and the following observations were made:

1. The annual collective dose equivalents rather than the dose equivalent commitments or the collective dose equivalent commitments for the predicted time of operation of the uranium mine of the Poços de Caldas region were calculated, because there were several intrinsic uncertainties in the parameters available for the calculations.
2. The fluctuations expected to occur in the data on populational distribution, irrigational practices, agricultural production, and food consumption in developing regions, like the Poços de Caldas plateau, make the quantitative assessment of the collective dose equivalent commitments meaningless, unless reliable long range predictions can be made on the varying parameters to enable time integration.
3. Linear models can be used to estimate the annual collective dose equivalents as a function of the ^{226}Ra concentration, based on parameters which may be valid at a particular time, but the actual collective dose equivalent commitment is difficult to predict.
4. Dosimetric models based upon site specific environmental models are helpful to estimate collective dose equivalents to populations from a particular practice, but extreme care should be exercised by competent national authorities when using such estimates in decision-making processes.
5. Paragraphs 22, 219, 221 and 232 of ICRP26 should be taken into full account when estimating collective dose equivalents."

In spite of the shortcomings involved in the application of the concepts of collective dose equivalent, dose-equivalent commitment and commited dose equivalent to uranium mining and milling, one must bear in mind that the accepted aims of radiation protection are:

(i) to prevent detrimental non-stochastic(*) effects, and
(ii) to limit the probability of stochastic(**) effects to an acceptable level.

(*) Non-stochastic effects are defined by the ICRP Publication 26 (1977b) as "those for which the severity of the effect varies with the dose, and for which a threshold may therefore occur".

(**) Stochastic effects are defined by the ICRP Publication 26 (1977b) as "those for which the probability of an effect occurring, rather than its severity, is regarded as a function of dose, without threshold.

On the one hand, the detriment in a population is defined by the ICRP Publication 26 (1977b) as "the mathematical expectation of the harm incurred from an exposure to radiation, taking into account not only the probability of each type of deleterious effect, but also the severity of the effect." On the other hand, the concept of detriment is tentatively related to the collective dose equivalent (see paragraph 22 of ICRP Publication 26, quoted earlier); and further according to the ICRP Publication 26 (1977b) "the assessment of the total population detriment due to radiation from a given exposure should also take account of the total risk of hereditary damage that may be expressed in all subsequent generations". Thus, based upon this series of concepts introduced by the ICRP a risk assessment becomes mandatory for radiation protection of populations.

7.2.1. Risk Assessment and Cost-Benefit Analysis

Here it must be mentioned that this work restricts itself to address the problem of risk assessment for ^{226}Ra releases from uranium mining and milling operations. The ICRP Publication 24 (1977a) discusses occupational risks and radiation protection of workers in uranium and other mines.

The system of risk assessment as devised in ICRP 26 (1977b) may be used as the basis to evaluate the potential total population detriment from human intake of ^{226}Ra from uranium mining and milling operations.

It should be emphasised here that the systems of dose limitations recommended earlier by the ICRP (1960), based upon a body burden of 0.1 μCi^{226}Ra, had already an assumed risk built into them deemed to be acceptable to the individual and to society in view of the benefits derived from activities, such as uranium mining and milling, involving exposure to ionizing radiation.

Thus, the concept of acceptable risk is implicitly used when the dose limitation system of a country for ^{226}Ra is based on calculating the dose as a fraction of either of the $(MPC)_w$ introduced by the ICRP Publication 2 (1960) or the Annual Limits on Intake (ALI) as recommended by the ICRP Publication 30 (1979b, 1980).

The ALI of a radionuclide is a secondary limit designed to meet the basic requirements for limiting occupational exposure. Accordingly the ALI of a radionuclide is the greatest value of the annual intake I which satisfies the following inequalities (ICRP 1979b):

$$I \sum_T \omega_T \, (H_{50,T} \text{ per unit intake}) \leqq 0.05 \text{ Sv} \qquad (3)$$

and

$$I(H_{50,T} \text{ per unit intake}) \leqq 0.5 \text{ Sv} \qquad (4)$$

where I(in Bq) is the annual intake of the specified radionuclide either by ingestion or inhalation; ω_T is the weighing factor for tissue (T) and has value as shown in Table 7.2.; and $H_{50,T}$ per unit intake (in Sv Bq^{-1}) is the committed dose equivalent in tissue (T) from intake of unit activity of the radionuclide by the specified route for 50 years after intake.

The ICRP Publication 30 (1979b) considered the period of 50 years as appropriate for an occupational lifetime, and emphasised that the $H_{50,T}$ is "the dose equivalent which a Reference Man is assumed to receive if he lives for 50 years after his intake of the radioactive material and if no steps are taken to accelerate the removal of the radionuclide from his body.

According the the ICRP Publication 26 (1977b): "a review of the radiosensitivity of bone in relation to the development of radiation-induced cancer indicates that, per unit dose equivalent, it is much less sensitive than breast, red bone marrow, lung and thyroid. For purposes of radiation protection the risk factor for bone cancer is taken to be 5×10^{-4} Sv^{-1}".

Table 7.3. presents the risks per unit dose. The ICRP risks are related to the weighting factors ω_T presented in Table 7.2. and used in equation (3) to estimate the ALI.

The ICRP in its publication 26 (1977b) inferred that the continuance of the former genetic dose limit of 5 rem in 30 years from all sources additional to the dose from the natural background radiation and from medical procedures (ICRP 1966c) could be understood as a suggestion of "the acceptability or a higher population exposure than is either necessary or probable, and a higher risk than is justified by any present or easily envisaged future development".

Assuming that risks regularly accepted in everyday life could be considered as a basis for the level of acceptability for fatal risks to the general public, and taking into account that the latter are an order of magnitude lower than for occupational risks, the ICRP Publication 26 (1977b) considered that "a risk in the range of 10^{-6} to 10^{-5} per year would be likely to be acceptable to any individual member of the public." Taking into account this range for fatal risk, the ICRP (1977b) estimates that "the application of an annual dose-equivalent limit of 5mSv to individual members of the public is likely to result in average dose equivalent of less than 0.5mSv, provided that the practices exposing the public are few and cause little exposure outside the critical groups".

The risk assessment procedures proposed by the ICRP Publication 26 is in essence the result of an evolution in concepts. The concern with the prevention of occurrence of health effects (assumed to be non-stochastic at first) in the ICRP Publication 1 (1959) soon developed in the recommendations of the ICRP Publication 2 (1960) and ICRP Publication 9 (1966c) states in its paragraph 47 after initial considerations that:"...The risks to members of the public from man-made sources of radiation should be less than or equal to other risks regularly accepted in everyday life, and should not be justifiable in terms of benefits that would not otherwise be received." Unfortunately, the ICRP recommendations could not resolve the imprecisions regarding the recipients of risks and the benefits, mainly when the exposure to radiation were not medical purposes. Trying to improve the effectiveness of the statement, the ICRP added in paragraph 52 of Publication 9 the following: "as any exposure may involve some degree of risk, the Commission recommends that any unnecessary exposure be avoid, and that all doses be kept as low as readily achievable, economic and social considerations being taken into account." This recommendation was further elaborated at the end of paragraph 7 of the ICRP Publication 22 (1973) as follows: "...The word possible has been successively replaced by practicable and readily achievable. The recommendation (i.e., paragraph 52 of ICRP Publication 9) has also been expanded to identify two specific considerations that are to be taken into account in determining levels of exposure that may be considered as low as readily achievable. These considerations are economic and social. Other considerations, such as ethical ones, are not excluded by this wording and may indeed be considered to be included by the adjective social."

The techniques of cost-benefit analysis to conform dose reductions recommended in the paragraphs 47 and 52 of ICRP Publication 9 and paragraph 7 of ICRP Publication 22 were described and discussed in Appendices II and III of ICRP Publication 22. However, the ICRP Publication 26 published in 1977 supersede the ICRP Publication 22. The system of dose limitation suggested in the ICRP Publication 26 has been (IAEA 1979a) and still is (IAEA 1981) under discussion by the IAEA and other international organizations.

The cost benefit methodology has been used for a long time in restricted cases of economics based upon previous studies in cost-effectiveness. However, the application of the cost benefit analysis to the field of radiation protection implied some degree of extrapolation as well as a built in cost-effectiveness in the cost curve associated with the collective dose equivalent. The differential cost-benefit analysis has been interpreted in radiation protection as a cost-effectiveness analysis in such a way that the cost curves should be made up of options which are themselves cost-effective (Beninson 1977, Webb 1979).

The ICRP Publication 26 (1977b) defines the net benefit B of a product or an operation involving irradiation as

$$B = V - (P + X + Y) \qquad (5)$$

where V is the gross benefit; P is the basic production cost (excluding protection); X is the cost of achieving a selected level of production; Y is the cost of the detriment involved in the operation or in the production, use and disposal of the product; and the word cost includes both social and purely economic costs.

The ICRP Publication 26 considers on the one hand the increase of benefit from a "reasonably achievable" radiation exposure and, on the other hand, the increase of cost in the achievement of this increase of benefit. The maximization of B in equation (5) in relation to the independent variable collective dose equivalent S from a practice is considered to correspond to the attainment of the optimum net-benefit B, so that:

$$\frac{dV}{dS} - \left[\left(\frac{dP}{dS} + \frac{dX}{dS} + \frac{dY}{dS}\right)\right] = 0 \qquad (6)$$

Considering now V and P as constants in relation to S for a given practice, the optimum net benefit B is attained at a values such that

$$\left[\frac{dX}{dS}\right]_{S*} = - \left[\frac{dY}{dS}\right]_{S*} \qquad (7)$$

The IAEA Safety series No. 45 (IAEA 1978) examines in great detail the application of the optimization techniques to determination of discharge limits. In particular, this IAEA publication makes special considerations inherent in the application of cost benefit techniques, and in its paragraphs IV-26 to IV-29 states the following:

> "IV-26. The finite nature of expenditures for current health protection or risk reduction provides a useful index for comparison, but these expenditures may not be strictly proportional to the collective detriment to the population as they are determined by political and social processes. Use has recently been made, however, of an assumed range of acceptable values for expenditures for risk reduction to establish radiation standards(*). Direct estimates have also been made of the worth that professionals in the radiation protection field would assign to a unit of collective dose (dollar/man-rem)(**). These estimates apply only uniform whole-body irradiation and equivalent estimates may be required for the cost of the detriment from collective dose commitments in other organs. These costs would be expected to be correspondingly smaller for other organs because of the lower detriment per rem for partial body irradiation.
>
> IV-27. Since the monetary value of radiation exposure reductions might vary among nations, national authorities might have to determine these values for their own population protection, but hopefully, an acceptable internationally agreed-on approach can be developed for global commitments. Care should be exercised when using a monetary value for the unit radiation detriment or unit collective dose commitment that is not out of proportion to implicit or explicit values in use for other sources order to use cost-benefit technique to their greatest potential.
>
> IV-28. All humans activities involve some inequities in the distribution of benefits and detriments to different population groups. For example, the general public incurs the detriment from automobile emissions, and pedestrians are subjected to higher risks without receiving direct benefits. Similar situations exist for radiation exposure. For example, individuals residing near a fuel fabrication facility may not receive any of the primary benefits from this practice, i.e. the electric power generated by the fuel. Secondary benefits such as those deriving from tax payments by the facility might accrue to the local population, but the primary benefits from the practice might be only received by a distant group that does not receive any of the detriment. The release of long-lived radionuclides to the environment, as, for example, from spent fuel reprocessing plants could result in detriments received by the world's

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(*) The U.S. Environmental Protection Agency (USEPA) recently used a range of values for risk reduction of US$ 200 000 - US$ 500 000 per projected serious health effect eliminated in establishing environmental radiation standards for normal releases from US facilities comprising the nuclear fuel cycle (USEPA 1977).

(**) The values reported (1976) for both methods of determination range between US$ 10 and US$ 980 (Otway 1972). The US Nuclear Regulatory Commission (USNRC 1975) has used a conservative interim value of US$ 1000/man rem reduction for the purpose of cost-effectiveness analysis of light-water reactor effluent reduction.

population, while the primary benefits are received by only some groups in one nation. Lastly, the genetic detriments from radiation exposure will be received by future generations and not the immediate individuals receiving the primary benefits.

IV-29. These inequities in the distribution of benefits and detriments in society are mitigated by regulatory authorities which establish limits on individual activities (air pollution emission criteria, traffic safety regulations, etc.), so that no group is subjected to excessive detriment. For radioactive material releases, the use of the collective detriment concept, that is the global collective dose commitment, and maintenance of all individual exposures within the ICRP limits, will ensure that the detriments are considered in the justification of the activity and that no single group will bear a severe detriment".

These four paragraphs define the IAEA position regarding the application of cost-benefit techniques.

Other national and international organizations address also to the problem of assigning a monetary value to the reduction of a collective dose of one person-rem.

The ICRP Publication 22 (1973) discusses briefly the relative importance of intangibles such as aesthetic, human and environmental factors in cost-benefit analysis, and lists estimates of monetary values of avoiding the detriment possibly associated with a population or collective dose of one person-rem with a range of US$10 to US$250 per person-rem.

The USNRC (1976) made an economic analysis and cost-benefit balancing for the economic impact of six alternative dispositions of plutonium. A comparison between alternative 6 (no reprocessing, no recycle) and alternative 3 (prompt uranium, and plutonium recycle) shows that a relatively small decrease in the radiological dose commitment would occur for alternative 6 as compared to the US$ 3.2×10^9 (1976 US$) worth fuel cycle cost of alternative 3. Trying to quantify a radiological impact decrease, this USNRC report (the GESMO report) states that a high, or maximum, value for the impact can be assessed by using the upper value for a person.rem suggested in the 10 CFR Part 50, Appendix I, at US$ 1000/person.rem.

One single assigned monetary value acceptable internationally seems to be unlikely, at least for the time being. A cost-benefit analysis applied as an excercise to building materials with comparatively high natural radionuclide concentration considered US$ 10 (7.5 roubles)/person.rem a more acceptable monetary value than US$ 250 (188 roubles/person.rem (Krisium and Karpov 1980). While previously, a risk and cost-effectiveness analysis applied to radioactivity in foods in the United States adopted a monetary value of US$ 15/person.rem of thyroid exposure based upon US$ 100 for the overall somatic health cost to the American society per person.rem (Shleien 1975).

Taking into account (i) all difficulties in evaluating (or at least interpreting) the net benefit mainly when the risks and benefits associated with a practice are not applied to the same subject, and (ii) the wide variation in the range of monetary values assigned to a collective dose of one person.rem, national authorities should exercise extreme care to avoid using the estimated net benefit and a cost reduction criterion as non-written ethical guides for decision-making processes involving the nuclear industry and other sources of radiation exposure.

Direct applications of the concepts of net benefit and cost reduction associated with radiation protection involving present uranium mining and/or milling operations were not available in the open literature at the time this report was prepared. However, an effort is expected to improve the use of such concepts for the radiological impact assessment of future uranium mining and milling operations. Difficulties in calculating collective dose equivalent commitments inherent in the fact that uranium mines are sometimes located in sites of developing regions with fast changing parameters like population distribution, irrigational practices, agricultural production and food consumption should not be underestimated (Paschoa et al. 1980). However the usefulness of concepts like risk assessment and cost-benefit analysis should not be ruled by national authorities. In applying such concepts the national authorities should be aware that improvements are still needed for the actual applicaton of some of these concepts, as mentioned for example, in the paragraph IV-27 of the IAEA document or the principles for establishing limits for the release of radioactive materials into the environment (IAEA 1978) quoted earlier in this section.

7.3. NATIONAL STANDARDS

There are a number of national standards for limiting radiation exposure from ^{226}Ra in waters.

7.3.1. General Objectives

The general objectives of national standards as understood here are to observe the limitations of radiation exposure, taking into account the basic and operational principles of radiation protection. Most national legislations on radiation protection reflect earlier recommendations of the ICRP.

The basic principles underlying the recommendations of ICRP are stated in the paragraph 2 of Publication 9(1966c) as follows:

"The policy adopted by the Commission in preparing its recommendations is to consider the fundamental principles upon which appropriate radiation(*) protection measures can be based, while leaving to the various national protection bodies the responsiblity of formulating the specific advice, codes of practice of regulations that are best suited to the needs of their individual countries. The Commission wishes to emphasize that its recommendations are intended to guide the experts responsible for putting radiation protection into practice. Because of their advisory character, the form in which the recommendations are worded will not necessarily be suitable for direct assimilation into regulations or codes of practices."

(*) The word "radiation" refers exclusively to <u>ionizing</u> radiation.

The IAEA Safety Series No. 45 (1978) states the objectives of radiation protection for environmental releases of radioactivity with basis on the ICRP Publications 22 and 26 (1973, 1977b). In particular, the paragraph I-3 of the IAEA publication (1978) reads as follows:

"I-3. The basic objectives of radiation protection are to prevent the occurence of acute effects and to limit the probabilities of occurrence of late somatic and genetic effects to levels deemed to be acceptable. The first of these objectives is easily met since acute effects occur only subsequent to large doses as high dose rates. The second objective relates to much more complicated problems, mainly due to the absence of human data at the levels of exposure which are currently permitted. It has been the normal practice in radiation protection to assume that a non-threshold direct proportionality relationship exists between the dose and the probability of such late effects as the induction of malignancies and deleterious hereditary effects. Furthermore, it is assumed that the risk per unit dose deduced from observations as high doses and dose rates apply to the low dose range and low dose rates relevant for radiation protection. Thus, for small dose increments above natural background, it may be assumed as a first approximation that the increment of risk is proportional to the increment of dose(*). This assumption may, however, not necessarily form the most appropriate basis for estimates of the actual risk associated with the low dose".

The 1977 UNSCEAR report (1977) mentioned, as a remark made by Kristan, Kobal and Legat (1974), that ^{226}Ra should be considered the most significant nuclide in water releases from uranium mining and milling operations. However, an up to date UNSCEAR working paper (1981), still unpublished at the time this present report was being prepared, considers that today's practice is to contain all uranium mining and milling liquid effluents and either partially recycle or evaporate the water. Furthermore, this UNSCEAR (1981) working paper asserts that there is essentially no liquid discharges or radiological significance from uranium mining and milling, and refers, in support of this assertion, to environmental surveys made in the United States in regions of hot and dry climate (Snelling and Shearer 1969, Snelling 1970, 1971). Here one should not deemphasize that there is still the possibility of human exposure to ^{226}Ra through ingestion of drinking water or food irrigated with waters contaminated by liquid effluents of uranium mining and milling.

Studies on the biological cycle of ^{226}Ra (Kirchmann et al. 1975) and this present IAEA coordinated research program have brought up enough experimental evidences to show that a comprehensive dose assessment of all stages of the nuclear fuel cycle should include, a fortiori, the potential contribution to human exposure from the ^{226}Ra content of the releases from uranium mining and milling.

(*) Under this assumption, each probability p_{ij} of suffering an effect i, in a population group j, will be directly proportional to the average dose in the range of interest

$$p_{ij} = r_{ij} \bar{H}_j$$

where r_{ij} is a risk factor, the value of which is not known with certainty, and $\bar{H}_j$ is the per caput dose received by individuals in the group j.

The main criteria used in general to establish national standards for liquid releases of radionuclides into the environment are the following: maximum permissible concentration in water $(MPC)_w$; annual limit of intake (ALI); maximum permissible dose (MPD); and maximum permissible discharge of radionuclides based upon factors determining the environmental capacity for receiving liquid releases from nuclear facilities.

7.3.2. Comparison of National Standards

An overall comparison of national legislations of nineteen countries on protection against ionizing radiation has been made by the World Health Organization (WHO 1972). The IAEA and WHO organized a meeting with the support of UNEP in 1974 on the population dose evaluation and standards for man and his environment, where many views and criteria on population exposure were presented (IAEA 1974). More recently an IAEA topical seminar on the practical implications of the ICRP Publication 26 recommendations and the revised IAEA basic standards was held in Vienna (IAEA 1979a). Some papers related to the application of the recommendations of the ICRP Publication 26 were presented in the fifth congress of the International Radiation Protection Association (IRPA 1980).

Table 7.4. summarizes the criteria adopted in a number of countries to establish national standards for liquid radioactive releases into the environment, and lists the limit values for ^{226}Ra whenever available in the literature consulted. Table 7.4. shows clearly that the criteria vary from country to country, depending mostly on the interpretation given by national authorities to the earlier ICRP recommendations.

On the one hand one can confidently say the recommendations of the ICRP Publications 2 and 9 (1960, 1966c) are tentatively followed in most countries, irrespective of differences in interpretation. on the other hand, the relatively new concepts introduced by the ICRP Publications 22 and 26 (1973, 1977b), and adopted as a policy by the IAEA (1978), have not yet permeate the national legislations as far as the ^{226}Ra dose limits are concerned. Whether or not the national standards will be altered according to the principles for establishing limits for the release of radioactive materials into the environment, as recommended by the IAEA (1978), is a matter to be considered by the competent national authorities. However, one must bear in mind, as mentioned earlier, that the concepts on which the present national standards are based, carry intrinsically an assumed risk deemed to be acceptable to the individual and to society in view of the benefits derived from activities such as uranium mining and milling.

7.4. SUMMARY AND CONCLUSIONS

The basic concepts associated with dose assessment for radiation protection were reviewed, taking into account the evolution of such concepts in the last 25 years. The difficulties in applying the relatively new concepts of collective dose equivalent commitment and commited dose equivalent to the case of uranium mining and milling were briefly examined.

Computational dosimetric models to biota were mentioned but not examined in any detail. Ranges of environmental dose rates to aquatic biota were given, however, there is a lack of a standardized methodology for calculating dose to biota.

The system of risk assessment as devised by the ICRP Publication 26 was discussed in view of the earlier ICRP Publication 2 recommended dose limits. The unescapable conclusion points out that the concept of acceptable risk is implicitly used when the dose limitation system for ^{226}Ra is based on calculating the dose as a fraction of either of the $(MPC)_w$ introduced by the ICRP Publication 2 or the ALI recommended by the ICRP Publication 30, the latter to be used only in the framework of the recommendations described in the ICRP Publication 26.

The technique of cost-benefit analysis was briefly presented and discussed as far as the assignment of a monetary value to the reduction of a collective dose of one person-rem is concerned. The main conclusions of the discussion just mentioned are the following:

(i) national authorities should exercise extreme care to avoid using the extimated net benefit and a cost reduction criterion as non-written ethical guides for decision-making processes involving the nuclear industry and other sources of radiation exposure;

(ii) the usefulness of concepts like risk assessment, collective dose equivalent, and cost-benefit analysis should not be ruled out by the national authorities; and

(iii) improvements are still needed for the actual application of some of the concepts introduced in radiation protection by the ICRP Publication 26.

Limitation of radiation exposure, taking into account the basic and operational principles of radiation protection is in the framework of national standards which reflect, in general, the recommendations of the ICRP. A review of the criteria adopted for each of a number of countries for establishing national standards was presented. Although the early ICRP recommendations (1960, 1966c) are usually incorporated in the national legislations, the most recent concepts introduced by the ICRP (1973, 1977b) and adopted as a policy by the IAEA (1978) are not used yet in the national standards for the ^{226}Ra dose limitation system.

A symposium to examine specifically the state of art of the dose limitation system for the case of uranium mining and milling should be jointly convoked by the IAEA, WHO, ICRP and UNEP in view of the fact that the national standards for ^{226}Ra dose limitation do not follow in general the IAEA adopted policy.

TABLE 7.1 Estimated collective dose commitment from uranium mining and milling operations.

	person-Gy/MWe.yr* — ref. [30] $\times 10^{-6}$												person.Sv/MWe.yr** - ref. [31] $\times 10^{-3}$	
	Ra-226			Th-230			U-238			Pb-210			GESMO†	APS††
	a	b	c	a	b	c	a	b	c	a	b	c	d or e	d or e
Mining	-	-	-	-	-	-	-	-	-	-	-	-	5.1	< 0.8
Milling	0.1	0.1	0.1	0.2	0.1	2	0.1	0.02	0.07	0.02	0.01	0.04	1.0	< 0.6

* Due to deposition on the ground, incurred mainly through the ingestion pathway but also including a contribution from inhalation of resuspended materials, and assuming the duration of the milling practice equal to 100 years.

** Associated to the incremental *per caput* annual dose rate for a world installed capacity of 1 kW *per caput* after many years of operation.

† GESMO = Final Generic Environmental Statement on the Use of Recycle Plutonium in Mixed Oxide Fuel in Light Water Cooled Reactors. U.S. Nuclear Regulatory Commission (NUREG-002) - cited in ref. [31] - assuming 50 years of operation.

†† APS = American Physical Society - ref. [31] - assuming 500 years of operation for the mills,and operation time depending on the deposit size and extraction rate for the mines.

a = lung (whole); b = bone marrow; c = bone lining cells; d = whole body; d = gonads.

TABLE 7.2 Weighting factors ω_T recommended by the ICRP for stochastic risks. From ref. [19].*

Organ and tissue	ω_T
Gonads	0.25
Breast	0.15
Red bone marrow	0.12
Lung	0.12
Thyroid	0.03
Bone surfaces**	0.03
Remainder***	0.30

*See also Table 7.3

**Relates to endosteal cells and to the epithelium on bone surfaces.

***a value of ω_T of 0.06 is applicable to each of the five organs or tissues of this remainder receiving the greatest dose equivalents and the exposure to all other tissues in this group is neglected. Skin and lens are not considered as part of the remainder tissue for limiting stochastic effects. When the gastrointestinal tract is irradiated, the stomach, small intestine, upper large intestine and lower large intestine are considered as four separate organs.

TABLE 7.3 Quantitative risk factors recommended by the BEIR [58]†, ICRP [17]* and UNSCEAR [30]†, taking into account age-and sex-dependency whenever it is significant.

Organ or tissue	Risk per unit dose (Sv^{-1})		
	BEIR	ICRP	UNSCEAR
Gonads	-	10^{-2}	-
Breast**	9.0×10^{-3}	2.5×10^{-3}	6.0×10^{-3}
Red bone marrow	2.5×10^{-3}	2.0×10^{-3}	$(1.5-2.5)\times10^{-3}$
Lung	3.9×10^{-3}	2.0×10^{-3}	$(2.5-5.0)\times10^{-3}$
Thyroid	-	5.0×10^{-4}	$(0.5-1.5)\times10^{-3}$
Bone	6.0×10^{-3}	5.0×10^{-4}	$(2.0-5.0)\times10^{-3}$
Pulmonary lymphoid	-	$2\ \times10^{-3}$	-
G.I. track	3.0×10^{-3}	-	2.5×10^{-3}
All other tissues	3.0×10^{-3}	$5\ \times10^{-3}$	2.5×10^{-3}

†Taken from ref. [59]

*The ICRP recommendations for dose limitations is based on the principle that the risk should be equal whether the whole body is irradiated uniformly or whether there is non-uniform irradiation. The condition $\sum_T \omega_T H_T \leq H_{wb.L}$ where ω_T is given in Table II and represents the proportion of the stochastic risk resulting from tissue (T) to the total risk, when the whole body is irradiated uniformly; H_T is the annual dose-equivalent limit in tissue (T); $H_{wb,L}$ is the recommended annual dose-equivalent limit for uniform irradiation of the whole body, namely 50 mSv (5 rem).

**Significant age-and sex-dependency.

Table 7.4 Criteria adopted to establish national standards for liquid radioactive releases, and the limit values for Ra-226 whenever available.

Country	Criteria	^{226}Ra limit	Succint description and/or remarks	Ref.
Australia	$(MPC)_w$	$10\ \mathrm{pCi}.\ell^{-1}$ $(0.37\ \mathrm{Bq}.\ell^{-1})$	ingested by a member of the public in the neighborhood of a mine or mill exposed continuously for 168 hours per week.	CDH** (1975)
Belgium	$(MPC)_w$	n.a.*	(i) for occupational exposure (168 - h. week) for discharges into the soil; (ii) (1/10) × $(MPC)_w$ for discharges into most surface waters, and into sewers and underground conduits.	WHO (1972)
	ALI	$1\ \mu\mathrm{Ci}.\mathrm{yr}^{-1}$ $(37\mathrm{K}\ \mathrm{Bq}\ \mathrm{yr}^{-1})$	estimated maximum dietary intake for a critical group of humans (i.e. 135 times the ICRP 1959 limit [1]).	Kirchmann (1975)
Brazil	ALI	$9.6\times10^{-3}\mu\mathrm{Ci}.\mathrm{yr}^{-1}$ (356 Bq)	per organ, based upon established MPD's for individual members of public - this limit is considered to be approximately equivalent to $10\ \mathrm{pCi}.\ell^{-1}$, depending upon drinking and dietary habits, and metabolic model.	CNEN*** (1973)
Bulgaria	$(MPC)_w$	n.a.	prohibit the discharge of liquid radioactive wastes into pits or wells or on to fields for irrigation purposes, as well as the discharge of waters contaminated with radioactive substances into body of water intended for pisciculture or the breeding of birds, or into watercourse flowing into such bodies of water.	WHO (1972)
Canada	$(MPC)_w$	n.a.	the permissible release rate of radionuclides is... in accordance with the results of environmental studies leading to knowledge of the dilution capacity of the environment, thus ensuring that the provisions relating to MPD to critical groups are fulfilled.	WHO (1972)
Czechoslovakia	$(MPC)_w$	n.a.	based upon the water use downstream from the release and a total annual release limit.	Sebesta et al.
Denmark	MPD	n.a.	efforts must be made at all times to ensure that radiation exposure is kept well below the maximum permissible doses and that the number of persons exposed is as small as possible.	WHO (1972)

Table 7.4 (cont. 2)

Country	Criteria	^{226}Ra limit	Succinct description and/or remarks	Ref.
Federal Republic of Germany	$(MPC)_w$	n.a.	water originating from controlled areas must not, if there is any possibility of its escaping, contain a concentration of radioactive substances higher than 1/10 of the $(MPC)_w$.	WHO (1972)
Finland	$(MPC)_w$	n.a.	facilities from which radioactive substance may be discharged into watercourses or groundwater may not be installed unless measured.	WHO (1972)
France	$(MPC)_w$	10 pCi.ℓ^{-1} (0.37 Bq ℓ^{-1})	drinking water must not have a radioactivity level greater than that laid down by the regulations in force and tests for radioactive elements must be carried out by laboratories approved by the Minister of Social Affairs after consulation with the Central Service for Protection against Ionizing Radiations;	WHO (1972)
			the $(MPC)_w$ for soluble radium concerns only to the drinking water, not to the liquid releases.	Canet Zettwoog
India	$(MPC)_w$	n.a.	from considerations of radiotoxicity the average intake of ^{226}Ra near the uranium ore processing facility of Juduguda, Bihar is much below permissible intake.	Iyengar Markose (1970a)
Italy	$(MPC)_w$	n.a.	the MPD's to the various organs and tissues and the $(MPC)_w$ for radionuclides in drinking water for three kind population categories are prescribed according to the pertinent international standards.	WHO (1972)
Japan	$(MPC)_w$	10 pCi.ℓ^{-1} (0.37 Bq ℓ^{-1})	the concentrations of ^{226}Ra in the drinking water and river in the vicinity of the uranium mining and milling sites are monitored periodically.	Iwata (undated)
Netherlands	$(MPC)_w$	10 pCi.ℓ^{-1} (0.37 Bq ℓ^{-1})	in the case of discharge into water the concentration at the point of discharge is less than 10 pCi.ℓ^{-1} for substances emitting alpha radiation.	WHO (1972)

Table 7.4 (cont. 3)

Country	Criteria	^{226}Ra limit	Succint description and/or remarks	Ref.
Spain	$(MPC)_w$	n.a.	the $(MPC)_w$ of radioactive isotopes in drinking water are 1/10 of those prescribed for controlled areas.	WHO (1972)
South Africa	MPD	n.a.	in the case of waste disposal of radioactive material meticulose care shall be taken by the holder of the authority in the disposal of radioactive waste, and such disposal shall be made only in a manner approved by the Atomic Energy Board from time to time, either generally or in any particular case.	WHO (1972)
Sweden	$(MPC)_w$	n.a.	maximum permissible discharges of radioactive substances into waters are formally subject to decision by the Crown (which delegates this function to the National Institute of Radiation Protection acting in consultation with the Environmental Protection Agency) in connexion with the authorization procedure under the Atomic Energy Law.	WHO (1972)
Switzerland	$(MPC)_w$	n.a.	the concentration of radioactive substances contained in the waste waters of an undertaking must not exceed the prescribed values.	WHO (1972)
USSR	$(MAPC)_w$	n.a.	$(MAPC)_w$ = mean annual permissible concentration in water; MPI = maximum permissible annual intake - the annual intake of radioactive isotopes by the body, rather than their mean daily concentration in water shall be determinant in evaluating the exposure dose to individual members of the public.	WHO (1972)
U.K.	$(MPC)_w$	n.a.	standards do not have any legal force as such in the United Kingdom, however, they may be taken into consideration by government inspectors in their overall assessment of an establishment.	WHO (1972)
United States of America	$(MPC)_w$	3 pCi.ℓ^{-1} (0.11 Bqℓ^{-1})	U.S. Public Health Service 1962 limit for the ^{226}Ra concentration in driking water, without mentioning ^{228}Ra.	USPHS (1962)
		5 pCi.ℓ^{-1} (0.19 Bqℓ^{-1})	U.S. Environmental Protection Agency current limit for combined concentration of ^{226}Ra and ^{228}Ra in community water systems.	USEPA (1975)

Table 7.4 (cont. 4)

Country	Criteria	^{226}Ra limit	Succint description and/or remarks	Ref.
United States of America	$(MPC)_w$	15 pCi.ℓ^{-1} (0.56 Bq ℓ^{-1})	U.S. Environmental Protection Agency current limit for gross alpha particle activity (including ^{226}Ra but excluding radon and uranium).	USEPA (1975)
Yugoslavia	ALI	9.6×10^{-3} μCi.yr^{-1} (356 Bq yr^{-1})	maximum permissible annual intake by ingestion for member of the public — this limit is estimated to be equivalent to a $(MPC)_w$ of 4 pCi ^{226}Ra.ℓ^{-1} in rivers with fish.	Kristan et al. (1974)

*n.a. = not available in the literature consulted.
**Commonwealth Department of Health
***Comissão Nacional de Energia Nuclear

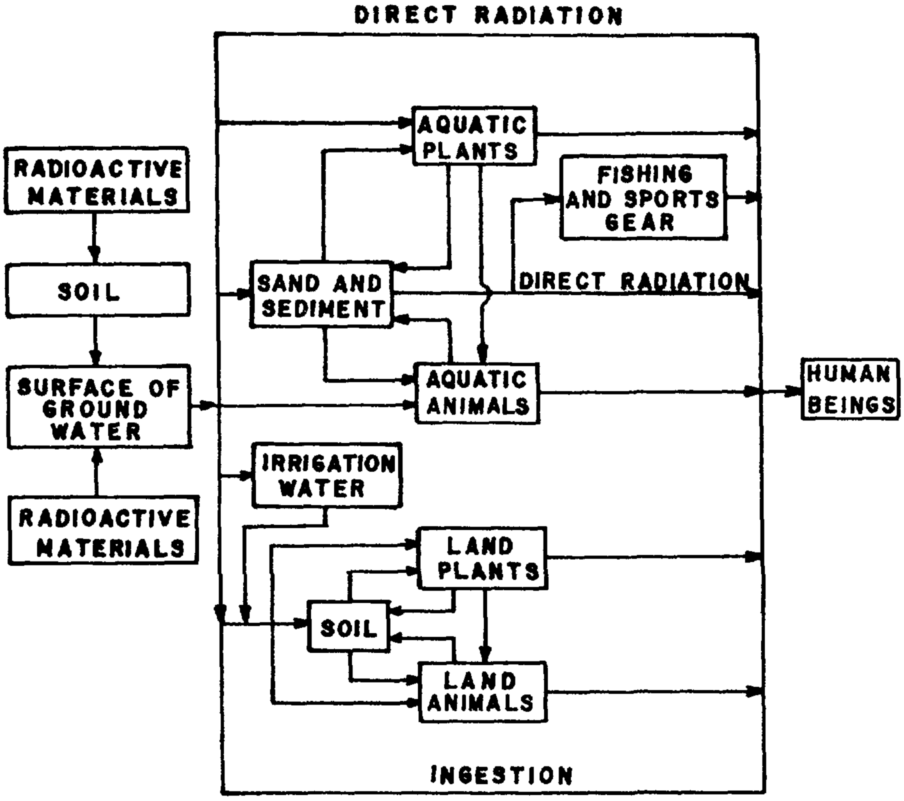

Fig.7.1 Simplified pathways between radioactive materials released to ground or surface waters and human beings. From ICRP 29 (1979a) p. 3.

REFERENCES

AMERICAN PHYSICAL SOCIETY,
LWR-assessment of radiation exposure, Report to the APS by the Study Group on Nuclear Fuel Cycle and Waste Management,
Reviews of Modern Physics 50 1 PII (1978) 571.

BENINSON D.,
Implementation of radiation protection requirements in the limitation of the release of radioactive effluents,
Application of Environmental Impact Analysis to the Nuclear Power Industry (Proc. Reg. Semin. Buenos Aires, 1977) IAEA-212, Vienna (1978) 37.

BLAYLOCK B.G., WITHERSPOON J.P.,
Dose estimation and predition of radiation effects on aquatic biota resulting from radioactive releases from the nuclear fuel cycle,
Impacts of Nuclear Releases into the Aquatic Environment (Proc. Symp. Otaniemi, 1975) IAEA, Vienna (1975) 377.

BROWNSCOMBE A.J., DAVY D.R., GILES M.S., WILLIAMS A.R.,
Three baseline studies in the environment of the uranium deposit at Yeerlirrie, Western Australia,
Australian Atomic Energy Commission, AAEC/E442, ISBN 0 642 59650 6 (1978).

CANET A., ZETTWOOG P.,
private communication.

COHEN B.L.,
The cancer risk from low-level radiation,
Health Phys. 39 (1980) 659.

COMISSAO NACIONAL DE ENERGIA NUCLEAR,
Normas Basicas de Proteçao Radiologica,
Resoluçao CNEN - 6/73 (1973) 100 pp.

COMMONWEALTH DEPARTMENT OF HEALTH,
Code of Practice on Radiation Protection in the Mining and Milling of Radioactive Ores,
Canberra, A.C.T. (1975).

DE JESUS A.S.M., MALAN J.J., BASSON J.K.,
private communication.

HAVLIK B.,
Radioactive pollution of rivers of Czechoslovakia,
Health Phys. 19 (1970) 617.

HAVLIK B., GRAFOVA J., NYCOVA A.,
Radium-226 liberation from uranium ore processing mill waste solids and uranium rocks into surface streams - I.
Health Phys. 14 (1968a) 417; II., Health Phys. 14 (1968b) 423.

INTERNATIONAL ATOMIC ENERGY AGENCY,
Population Dose Evaluation and Standards for Man and His Environment (proc. Sem. Portoroz, 1974), IAEA, Vienna (1974) 648 pp.

INTERNATIONAL ATOMIC ENERGY AGENCY,
Effects of Ionizing Radiation on Aquatic Organisms and Ecosystems, Technical Reports Series No. 172, IAEA, Vienna (1974) 648 pp.

INTERNATIONAL ATOMIC ENERGY AGENCY,
Principles for Establishing Limits for the Release of Radioactive Materials into the Environment,
Safety Series No. 45, IAEA, Vienna (1978) 91 pp.

INTERNATIONAL ATOMIC ENERGY AGENCY,
Practical Implications of the ICRP Recommendations (1977) and Revised IAEA Basic Standards for Radiation Protection.
(Proc. Top. Semin. Vienna, 1979) IAEA/ILO/WHO/OECD/ICRP, Vienna (1979a).

INTERNATIONAL ATOMIC ENERGY AGENCY,
Methodology for Assessing Impacts of Radioactivity on Aquatic Ecosystems,
Technical Reports Series No. 190, IAEA, Vienna (1979b) 416 pp.

INTERNATIONAL ATOMIC ENERGY AGENCY,
Application of the Dose Limitation System in Nuclear Fuel Cycle Facilities and Other Radiation Practices,
(Int. Symp. Madrid, 1981). IAEA/WHO/OECD/ICRP (In press).

INTERNATIONAL COMMISSION ON RADIATION UNITS AND MEASUREMENTS,
Conceptual Basis for the Determination of Dose Equivalent
(ICRU Report 25), Washington, D.C. (1976) 21 pp.

INTERNATIONAL COMMISSION ON RADIATION UNITS AND MEASUREMENTS,
Radiation Quantities and Units
(ICRU Report 33). Washington D.C. (1980) 25pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Recommendations of the International Commission on Radiological Protection
(ICRP Publication 1) Pergamon Press (1959).

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Report of ICRP Committee II on Permissible Dose for Internal Radiation (1959), with Bibliography for Biological, Mathematical and Physical Data
(ICRP Publication 2), Health Physics 3 (1960) 380 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Principles of Environmental Monitoring Related to the Handling of Radioactive Materials.
(ICRP Publication 7), Pergamon Press, Oxford (1966a) 11 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
The evaluation of Risks from Radiation,
(ICRP, Publication 8) Pergamon Press, Oxford (1966b) 60 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Recommendations of the International Commission on Radiological Protection,
(ICRP Publication 9) Pergamon Press, Oxford (1966c) 27pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Implications of Commission Recommendations that Doses be kept as Low as Readily Achievable,
(ICRP Publication 22) Pergamon Press, Oxford (1973) 18 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Radiation Protection in Uranium and Other Mines
(ICRP Publication 24), Annals of the ICRP, Pergamon Press, Oxford 1 1 (1977a) 28 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Recommendations of the International Commission on Radiological Protection,
(ICRP Publication 26), Annals of the ICRP, Pergamon Press, Oxford 1 3 (1977b) 53 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Radionuclide Release into the Environment: Assessment of Doses to Man.
(ICRP Publication 29), Annals of the ICRP, Pergamon Press, Oxford, 2 2 (1979a) 76 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Limits for Intakes of Radionuclides by Workers.
(ICRP Publication 30, Part I), Annals of the ICRP, Pergamon Press, Oxford, 2 3/4 (1979b) 116 pp.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION,
Statement and Recommendations of the 1980 Brighton Meeting of the ICRP - Limits for Intakes of Radionuclides by Workers.
(ICRP Publication 30, Part 2) Annals of the ICRP, Pergamon Press, Oxford, 4 3/4 (1980) 71 pp.

INTERNATIONAL RADIATION PROTECTION ASSOCIATION,
(Proc. Conf. Jerusalem 1980) Vol. III (1980).

IWATA I., KITAHARA Y., TAKENAKA S., KUROKAWA Y.,
Mill tailings disposal and environmental monitoring at the Ningyo-Toge uranium processing pilot plant,
Power and Nuclear Fuel Development Corporation, Tokyo (undated).

IYENGAR M.A.R., MARKOSE P.M.,
An investigation into the distribution of uranium and daughters in the environment of a uranium ore processing facility,
Radiation and Radioisotopes in Soil Studies and Plant Nutrition (Proc. Symp. Bangalore, 1970). Department of Atomic Energy (1970 a) 143.

IYENGAR M.A.R., MARKOSE P.M.,
Monitoring of the aquatic environment in the neighborhood of uranium mill at Jaduguda, Bihar,
Radiation Physics (Proc. Symp. Trombay, 1970b) 473.

KAUFMANN R.F., EADIE G.G., RUSSEL C.R.,
Ground water quality impacts of uranium mining and milling in the Grants Mineral Belt, New Mexico.
U.S. Environmental Protection Agency, E.P.A. 906/9-75-002 (1975).

KIRCHMANN R., LAFONTAINE A., CANTILLON G., BOULENGER R.,
Tranfert dans la chaine alimentaire de l'homme, du radium-226 provenant d'effluents industriels diversés dans les cours d'eau,
(Proc. Symp. Rome, 1971).

KIRCHMANN R., LAFONTAINE A., CARTILLON G., BOULENGER R.,
Etude du cycle biologique parcouru par la radioactivité.
Centre d'Etudes Nucléaires, Mol, BLG 477, Vol. II (1975) 124 pp.

KRISIUK E.M., KARPOV V.I.,
Cost-benefit analysis applied to building materials with comparatively high natural radionuclide concentration,
Health Phys. 39 (1980) 578.

KRISTAN J., KOBAL I., LEGAT F.,
Measurements of radon under various working conditions in the explorative mining of uranium
Population Dose Evaluation and Standards for Man and His Environment (Proc. Semin. Portoroz, 1974) IAEA, Vienna (1974) 217.

KUROKAWA Y., KUROSAWA R.,
private communication.

LECLARE P., HAIRR L., SCHMIRL L., PHILBIN T., STOECKER R., EISENBUD M.,
Standard methodology for calculating radiation dose to lower form biota,
Atomic Industrial Forum Inc., AIF/NESP-006 (1975) 109 pp.

MARPLE M.L., ZETTWOOG P.,
private communication.

MORGAN K.Z.,
History of damage and protection from ionizing radiation,
Principles of Radiation Protection (MORGAN, K.Z., TURNER, J.E., Eds.)
Robert E. Krieger Publishing Company, Huntington, New York (1973a) 1.

MORGAN K.Z.,
The need for radiation protection,
Radiological Technology 44 (1973b) 385.

NATIONAL ACADEMY OF SCIENCES (USA),
The Effects of Populations of Exposure to Low Level of Ionizing Radiation,
Report of the BEIR Advisory Committee, Washington, D.C. (1972) 217 pp.

OTWAY H.,
The quantification of social values, Risk-Benefit: Solution or Dream,
Los Alamos National Laboratory Rep. LA-4860-MS (Feb. 1972) 1.

PASCHOA A.S., BAPTISTA G.B.,
Method for calculation of upper limit internal alpha dose rates to aquatic organisms with application to plutonium-239 in plankton,
Health Phys. 35 (1978) 404.

PASCHOA A.S., BAPTISTA G.B., MONTENEGRO E.C., MIRANDA A.C., SIGAUD G.M.,
Ra-226 concentrations in the hydrographic basins near uranium mining and milling in Brazil,
Low-Level Radioactive Waste Management (Proc. Symp. Williamsburg, 1979) EPA 520/3-79-002 (1979a) 337.

PASCHOA A.S., BAPTISTA G.B., WRENN M.E., EISENBUD M.,
Dosimetry of natural and man-made alpha emitters in plankton,
Impacts of Radionuclide Releases into the Marine Environment (Proc. Symp. Vienna, 1980) IAEA, Vienna (1981a) 695.

PASCHOA A.S., SIGAUD G.M., MONTENEGRO E.C., BAPTISTA G.B.,
Ra-226 collective dosimetry for surface waters in the uranium mining region of Poços de Caldas
(Proc. 5th IRPA congress, Jerusalem, 1980) International Radiation Protection Association Vol. III (1980) 335.

PASCHOA A.S., SIGAUD G.M., BAPTISTA G.B., LATHAM E.C.H.Y.,
The concept of collective dose equivalent and the front end of the nuclear fuel cycle,
The Application of the Dose Limitation System in Nuclear Fuel Cycle Facilities and Other Radiation Practices (Proc. Symp. Madrid 1981) IAEA, WHO, OECD/NEA, ICRP, Vienna (1981b) In press.

PASCHOA A.S., WRENN M.E., EISENBUD M.,
Natural radiation dose to Gammarus from Hudson River,
Radioprotection 14 (1979b) 99.

PRADEL J., ZETTWOOG P.,
La radioprotection dans l'extraction et le traitement de l'uranium et du thorium.
(Proc. Symp. Bordeaux, 1974) Labour Office ed., Genève (1974) 249.

PRESTON A.,
The radiological consequences of releases from nuclear facilities to the aquatic environment,
Impacts of Nuclear Releases into the Aquatic Environment (Proc. Symp. Otaniemi, 1975) IAEA, Vienna (1975) 3.

SEBESTA F., BENES P., SEDLACEK J., JOHN J., SANDRIK R.,
private communication.

SHLEIEN B.,
A risk and cost effectiveness analysis of United States guidelines relative to radioactivity in foods,
Health Phys. 29 (1975) 307.

SIEK R.D.,
Review of environmental aspects of uranium mill operations.
Methods for Measuring Radiation in and Around Uranium (Workshop New York 1977).

SNELLING R.N.,
Environmental survey of uranium mill tailings pile, Monument Valley, Arizona,
Radiol. Health Data 11 (1970) 511.

SNELLING R.N.,
Environmental survey of uranium mill tailings pile, Mexican Hat, Utah, Radiol. Health Data 12 (1971) 17.

SNELLING R.M., SHEARER S.D.,
Environmental survey of uranium mill tailing pile, Tuba City, Arizona, Radiol. Health Data 10 (1969) 457.

TEMPLETON W.L.,
Ecological effects of transuranics in the marine environment, Radiation Effects on Aquatic Organisms (EGAMI, N., Ed.) Japan Scientific Society Press, Tokyo, University Park Press, Baltimore (1979) 3.

TILL L.E.,
The effect of chronic exposure to ^{238}Pu (IV) citrate on the embroyonic development of carp and fathead minnow eggs, Health Phys. 34 (1978) 333.

TSIVOGLOU E.C.,
Environmental monitoring in the vicinity of uranium mills, Radiological Health and Safety in Mining and Milling of Nuclear Materials, (Proc. Symp., Vienna, 1963) IAEA, Vienna (1963).

UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION,
General Assembly Records: 19th Session,
Supplement No. 14 (A/5814), U.N. New York, (1964).

UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION,
General Assembly Records: 21st Session,
Supplement No. 14 (A/6314), U.N. New York, (1966) 153 pp.

UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION,
Source and Effects of Ionizing Radiation.
(1977 Report to the General Assembly) United Nations (1977) 725 pp.

UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION,
Exposures resulting from nuclear power production,
Annex F, 30th session of UNSCEAR - Vienna 6-10 July 1981, A/AC.82/R. 386 (Unpublished).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY,
Interim primary drinking water regulations,
Title 40 of the United States Code of Federal Regulations, Federal Register 158, Washington, D.C., (1975) 34323.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY,
Environmental Radiation Protection Standards for Nuclear Power Operations,
Title 40 part 190, Code of Federal Regulations, Federal Register Vol. 42, No. 9 (13 Jan. 1977) 2858; and Final Environmental Statement on 40 CFR 190, Rep. No. EPA 520/4-76-016 (1976).

UNITED STATES NUCLEAR REGULATORY COMMISSION,
Opinion on Numerical Guidelines for Achieving as Low as is Reasonably Achievable Levels of Radioactive Materials in Light Water Reactor Effluents,
Federal Register Vol. 40, No. 137 (5 May 1975).

UNITED STATES NUCLEAR REGULATORY COMMISSION,
Final Generic Environmental Statement on the Use of Recycle Plutonium in Mixed Oxide Fuel in Light Water Cooled Reactor (GESMO), Summary, Vol. 1, NUREG-0002 (1976) 69 pp.

UNITED STATES PUBLIC HEALTH SERVICE,
Drinking Water Standards.
(USPHS Publication 956) Washington D.C. (1962).

WEBB G.A.M.,
Practical implementation of differential cost-benefit analysis in waste management studies,
Waste Disposal and Other Radiation Problems in Nuclear Industry (Proc. Summer School, Dubrovnik, 1979) (VUKOVIC, Z., Ed.) Boris Kidric Institute of Nuclear Sciences, Belgrade (1979) 240.

WOODHEAD D.S.,
Levels of radioactivity in the marine environment and the dose commitment to marine organisms,
Radioactive Contamination of the Marine Environment (Proc. Symp. Seattle, 1972) IAEA, Vienna (1973) 499.

WOODHEAD D.S.,
The estimation of radiation dose rates to fish in contaminated aquatic environments, and the assessment of the possible consequences,
Population Dose Evaluation and Standards for Man and His Environment (Proc. Semin. Portoroz, 1974) IAEA, Vienna (1974) 555.

WORLD HEALTH ORGANIZATION,
Protection Against Ionizing Radiations: A Survey of Current World Legislation,
Geneva (1972) 328 pp.

WRENN M.E.,
Internal dose estimates,
Areas of High Natural Radioactivity (Proc. Symp. Poços de Caldas, 1975, CULLEN, T.L., PENNA FRANCA, E., Eds.) Academia Brasileira de Ciências (1977) 131.

Chapter 8

POLLUTION ABATEMENT

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8.1. INTRODUCTION

The reports concerning radium removal techniques of aqueous solutions are presented by the delegations of several countries. These reports can be divided into two groups. One group concerns removal problems to reduce radium concentrations in underground drinking water supplies found in the United States. Another group is related to environmental hazard controls with the uranium mine operations in France, Japan and United States, etc.

8.2. RADIUM IN THE AQUEOUS ENVIRONMENT AND ITS REMOVAL

8.2.1. Levels of Radium-226 Groundwater Sources in U.S.A

Levels of Radium-236 are quite high in some groundwater sources throughout the United States. Most of this contamination is due to natural radioactivity as a result of aqueous leaching from uranium ores. Since control at the source is very difficult or impossible, attempts were made to remove the radioactivity from underground drinking water supplies. This was usually done when it was not practical to switch to another source of drinking water as in the case of well water supplies in small towns.

8.2.2. Radium Removal in Public Water Supply Systems

8.2.2.1. Removal using conventional water softening methods

In the state of Illinois, the U.S. Environmental Protection Agency (EPA) conducted a study to determine the efficiency of radium removal using conventional water softening methods (reference 1). The water softening equipment at these locations utilized both ion exchange and lime softening processes. Five locations were chosen with populations ranging from 235 to 58,000 people. The smallest water supply was the Dwight Correctional Center near the village of Dwight, Illinois. The other locations were at the city of Peru, (12,000), the village of Herscler (1,000), the city of Elgin (58,000), and the village of Lynwood (4,000). The Radium-226 levels in the raw water ranged from 3.3 to 14.7 pCi/l.

In general, the ion exchange softening process removed Radium-226 more efficiently (70.2% to 98.2%) as compared to 70% to 92% for lime softening. The advantage of the lime softener process was that there was not the problem of breakthrough as at the end of a run through an ion exchange system. Both systems, however, have the disadvantage of the need for disposal of radioactive solid waste. Significant amounts of radium are concentrated in the brine rinse and the lime sludges. They are discharged into sewers, watercourses or placed on land. Although this may not present a problem similar to the waste from uranium mines and mills, a more satisfactory solution should be found.

8.2.2.2. Removal using manganese-coated acrylic fibers

A more unique technique for removing radium from groundwater has been utilized in Texas. A contract was given by EPA to the state of Texas to determine the feasibility of using manganese-coated acrylic fibers to decontaminate groundwater with high levels of radium due to leaching of uranium ore bodies or to treat effluents from the uranium mining and milling industry. The study was conducted utilizing the water supply of Flatonia, Texas with a population of 1108 (reference 2). Radium-226 levels at four wells ranged from 3 to 16 pCi/l. If one filter stage is utilized, the process is at least 80% efficient. The recommendation of the study was that the efficiency of Radium-226 removal should be at least 95% which means using two filter stages. The cost of this process is about 45 US cents per thousand gallons of water being filtered. The cost of laboratory analysis, overhead, amortization and installation was not included.

The Flatonia study does not deal with the disposal problem of the acrylic filters. The filters could be immersed in nitric acid or a potassium salt and used again. However, then the radium is in a concentrated liquid phase which is a more difficult form for disposal. Persons experienced in health physics procedures would then be necessary at the water treatment plant which is not practical for a municipal utility. It may be that these filters could be buried in a land fill. This could be a potential contamination problem however. The state of Texas does not have a solution for this waste disposal problem.

8.2.3. Impact on Groundwaters of Uranium Mills

The U.S. Nuclear Regulatory Commission (NRC) has done an extensive study on the environmental effects of uranium mills (reference 3). One of the major concerns was the seepage of radioactive isotopes such as radium into groundwater supplies from active and inactive uranium tailings piles. Very few field studies have been conducted so a theoretical analysis by Rahn and Mabes (reference 4) was used by NRC to estimate the impact of contamination from tailings ponds. This study concluded that there would not be any contamination of groundwater from radioactive material. However, non-radioactive substances such as arsenic, selenium, molybdenum, cyanide, and chromium could contaminate water supplies over the lifetime of a uranium mill. After termination of mill operation, seepage would not continue since precipitation in the southwestern part of the United States is sparse.

Due to the potential contamination of groundwater supplies, the NRC require the uranium tailings piles to have clay or synthetic liners to prevent seepage during the operation of the mill. Other alternatives to control seepage such as dewatering and fixation were considered but are usually too expensive compared to the lining of the evaporation pond. Neutralization of the tailings can also be considered if the pond is located in an area where precipitation is greater than evaporation and thus provides a force for seepage after the mill ceases operation.

A field study by the EPA (reference 5) did confirm the NRC conclusion that radioactivity was not seeping very far from uranium mines and mills. None of the municipal supplies near the uranium mining and milling area had radium concentrations above the drinking water standard. The study concentrated on radionuclide contamination but the data did indicate there was selenium contamination of a domestic well in the area.

8.3. RADIUM POLLUTION ABATEMENT ON LIQUID EFFLUENTS FROM URANIUM MINES

Various types of radium-barium coprecipitation processes have been conducted by the owners of uranium mines. Some difficult problems of the coprecipitation process are the choice of solid waste disposal methods and sites to prevent radiological hazards, and the treatment of the residual harmful substances such as barium ions in process water since these materials may present new water pollution problems.

8.3.1. Information on French Experience

According to the French reports (references 6, 7, and 8), experiments have been carried out with the introduction of barium chloride solutions into a clarified effluent discharged from the tailings pond of uranium mine under various conditions. Sufficient sulfate content, (2 to 3 g/l), to allow complete precipitation of barium sulfate was present in the mine effluent. A sulfate content of 0.6 g/l is necessary to ensure removal of soluble radium. A mine effluent of about 450 pCi/l of Radium-226 was treated with 15 mg/l of barium chloride resulting in a final concentration of less than 5 pCi/l of Radium-226. The linear relationship between decontamination coefficient C (concentration of soluble radium in inlet water / concentration of soluble radium in outlet water) and an added amount of barium chloride was determined experimentally. For the purpose of efficient settling of barium-radium sulfate precipitation, effects of fatty organic acids and FA20-H (an anionic flocculent) were tested in a pilot pond. A settling efficiency of 75% was achieved in 2 hours of retention time with mechanical floculation by 11 baffles in the pond with the addition of 1.6 mg/l of FA20-H chemical flocculent. Under the same conditions, but using only 7 baffles, the settling efficiency was 57%. The efficiency was further reduced to 54% when the flocculent was not added. All experiments utilizing fatty organic acids as an additive indicated poor results. The barium concentration in the treated water was 0.2 - 0.8 mg/l.

8.3.2. Information on Japanese Experience

Similar reports (references 9 and 10) were provided by Japanese delegations. The radium removal techniques for the dam overflow or mine water of a Japanese uranium mine were presented. A barium chloride solution was added to the dam overflow at the rate of 0.05 kg of solution per cubic metre of dam overflow. The dam overflow containing enough sulfate for precipitation, radium in the water was coprecipitated with the barium. The experiments indicated that, when the addition of barium chloride was 0.02 kg/m^3, the radium concentration in the dam overflow (70 - 500 pCi/l) was reduced below 5pCi/l, and that, when 0.05 kg/m^3 of barium chloride was added to the water, the 0.5 pCi/l radium including treated water was achieved. However, a problem is developed since the primary effluent had barium sulfate particles which were so small in diameter as 1 to 2μm, that the sedimentation velocity is so low as 0.2 mm/min. Since it was technically difficult to separate the radium by a filtering process after the addition of barium chloride, 0.1 kg/m^3 of Bentonite was also added to form larger flocks to increase sedimentation. A concentration of 0.01 kg/m^3 of another precipitant was also added to increase the sedimentation velocity to 2.4 mm/min.

Recently, five settling ponds (total area 2200m^2) and ten sand filters (total area 930m^2) were constructed at radium decontamination facilities near the Ningyo-toge mine. Two such systems were provided to maintain sufficient treatment capacity (6m^3/min) during the heavy rainfall period. Each individual system had an effluent treating capacity of 1 m^3/min under ordinary conditions.

Another kind of experiment was performed to remove radium with barite minerals. The barite was supplied from a Japanese mine and estimated to have about 62% barium sulfate. Two sizes of barite blocks (10 to 32 mesh and 32 to 65 mesh), were prepared. Glass columns, which had a 29mm diameter, were filled with 300g of above these barite blocks. About 97% of radium in the mine water was removed at a flow-rate of 100 ml/min by using a column containing the large size barite blocks and 99.7% efficiency was reached with a flow rate of 5 ml/min by using the smaller blocks.

REFERENCES

[1] BENNETT D.L., BELL C.R. and MARKWOOD Ira M., Determination of Radium removal efficiencies in Illinois water supply treatment processes, Illinois Environmental Protection Agency, Technical Note ORP/TAD-76-2, Office of Radiation Programs, EPA Washington, D.C. 20460 (May 1976).

[2] COOK L.M., Advanced technology for radium removal from drinking water: The Flatonia Water Treatment Project, EPA Contract No. 68-01-3985, Division of Occupational Health and Radiation Control, Texas Department Health, Austin, Texas (1979).

[3] U.S. Nuclear Regulatory Commission, Final Generic Environmental Impact Statement on Uranium Milling, NUREG-0706, Vol. I-III, Office of Nuclear Material, Safety and Safeguards (September 1980).

[4] RAHN P.H. and MABES D.L., Seepage from uranium tailings ponds and its impact on ground water, Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico (July 1978).

[5] KAUFMANN R.F., EADIE G.G. and RUSSELL C.R., Effects of uranium mining and milling on ground water in the Grants Mineral Belt, New Mexico, Ground Water, Volume 14, Number 5 (September 1976).

[6] FOURNIER P.M., Current Research and development on Radium-226 Control at the French Atomic Energy Commission (1977).

[7] CANET A. and ZETTWOOG P., Elimination du radium des effluents d'usines de traitement de minerai d'uranium et d'eau d'exhaure de mines par le procédé au chlorure de Baryum (1977).

[8] CANET A., Etude en bassin pilote de la coprécipitation du radium soluble par le chlorure de barium et de la décantation du précipité des sulphates de baryum-radium, dans les effluents de l'usine SIMO-Vendée et dans l'eau d'exhaure de la mine de l'Ecarpière (1976).

[9] IWATA I., KITOHARA Y., TAKENAKA S., KUROKAWA, Y., Mill tailings disposal and environmental monitoring the Ningyo-toge uranium processing pilot plant, (1978).

[10] KUROKAWA Y., The Source, distribution, measurement and deposition of radium in Japan, (1976).

Chapter 9

ADMINISTRATIVE AND TECHNICAL ANNEXES

9.1. PURPOSE AND SCIENTIFIC SCOPE OF THE PROGRAMME

As indicated by the title, this programme was designed to develop systematic information on the form and movement of radium in water under a range of environmental conditions, this information being of great value to those authorities responsible for assessing the consequences of radium releases to water and to those responsible for setting discharge limits.

Scientific Scope

The scientific scope of this Coordinated Research Programme was given as follows:

"(a) Selection and standardization of methods for determination of radium in water. The methods must provide an acceptable method for differentiating between soluble and insoluble radium;

(b) The distribution of soluble and insoluble radium in natural waters and those affected by mining or milling operations will be studied, and the changes over time and distance will be determined. The cause of the changes should be elucidated. Deposition, sorption, resolution and resuspension phenomena will be studied;

(c) The factors affecting the leaching rate from ore heaps and tailings piles will be investigated. Of particular importance is the investigation of the effect of revegetation of tailings piles on the leach rate;

(d) The uptake of radium by biological systems, especially those which form part of man's food chain."

9.2. PROGRAMMES OF PARTICIPATING LABORATORIES

In order to fulfill the aims of the programme - development of systematic information on the source, distribution, movement and deposition of radium in inland waterways and aquifers - the role of laboratories was to carry out a variety of projects under a range of environmental conditions.

9.2.1. Australia

Two sub-coastal flood plains in northern Australia were examined for radium content and distribution. Both plains are subject to extensive annual flooding, they have uranium mineralization within their catchments and they both support a pastoral industry. Uranium has already been mined from the catchment of one plain and it was planned to begin mining in the second catchment in the near future.

The aim of the programme was to describe radium flow, both from natural arisings and from past mining operations, so that effluent standards and surveillance procedures could be set up and monitored when further uranium mining was embarked upon.

9.2.2. Brazil

In Brazil, the research objectives were the following:

1) Studies on the pH and radiochemical characteristics of water leaching of radium in tailings from uranium mining and milling operations;
2) Identification of the sources of Ra-226 in inland waterways in the Poços de Caldas region;
3) Investigation of the fate of Ra-226 produced in mining and milling operations in existing facilities and in their vicinities in relation to man's food chain;
4) Tentative evaluation of the population dose due to Ra-226 incorporated in the environment as a result of mining and milling operations.

9.2.3. Czechoslovakia

In Czechoslovakia, the research objectives were the following:

1) Selection, development and improvement of suitable methods for determination of radium and its chemical forms in water. These methods included emanometric, sorbemulsion, extraction, ultrafiltration, centrifugation, ion exchange and other methods;
2) Investigation of the chemical forms of existence of radium in selected natural waters in relation to the source of radium, distance from the source and hydrobiological conditions. Interpretation of the possible influence of individual factors;
3) Investigation and characterization of the distribution processes of radium in river or lake water, suspended particles and bottom sediments. Assessment of main factors influencing these processes;
4) Study of the uptake of different forms of radium by biological systems, especially those forming part of man's food chain, in relation to their health impact.

9.2.4. France

In France, a study programme was set up with the intention of preparing a document on the transport of radium from the beginning of treatment to the rivers and the ground. The programme contained four points:

1) Observation of radium in plant studies to determine the causes of the fluctuations observed in the concentration at the level of the discharge, and to investigate the possibility of accidental discharges during certain maintenance operations (resins, filter sludges, etc.). Examination of the conditions assuring minimum solubilization;

2) Study of the abatement of the radium in the basins. Study of the cost of reduction to 10pCi/l at the level of the discharge;

3) Neutralization trials in model plants with the water before and after transit into the basin;

4) Study of the consequences of the present discharge. Completion of the study by evaluation of the doses that reached the critical group of the population for the present discharges.

9.2.5. India

In India, three phases were planned:

1) First Phase:
   - (a) Survey of coastal discharges in the south, from Madras on the east coast to Mangalore on the west coast; sampling of coastal sediment and of the most common fishes;
   - (b) Comparison of the Madras thermal project residues of coal ash with original lignite samples;
   - (c) Examination at the mine site of effluents, drinking water, fish and dissolved and atmospheric radon; Search for indicator vegetation.
2) Second Phase:
   - (a) Chemical examination of samples (about 3-6 months);
   - (b) Sampling of air, dust, soil and plants in central and upper India regions (foot hill areas) in collaboration with the Division of Atomic Minerals; survey of phosphatic minerals and fertilizers;
   - (c) Dietary analyses; body burden measurements; drinking water, milk, diet, grass, soil-vegetation, grass-milk, sediment-fish relationships.
     Study of food chains and bioaccumulation.
3) Third Phase:
   - (a) Completion of analyses; Data analyses.
   - (b) Exposure evaluation
     - i) Calculation
     - ii) Urine and fecal examination of occupational workers.
     - iii) National average Ra burden.
   - (c) Confirmatory bone and teeth analyses.

This itemization indicates the line of approach and not a schedule. The programme of examination was also to determine the type, location and species of the organic-bound incorporated radium - whether it is easily labile in soil - and to determine the ecological relationships.

It was also of interest to find the influence of other elements and fertilizers on the lowering of radium intake. For example, the southern areas are known for the production of coconuts grown on beaches and fed by sandy soils. These soils often contain monazite. As a result, the coconut kernel and water have been found to contain radium.

9.2.5. Japan

In Japan, environmental surveillance for radium from uranium mining or milling operations is sufficient to ensure that the concentration in natural water is less than the regulation value, because environmental problems have recently come under stricter control in Japan. PNC plans to continue mining and milling operations at the Ningyo-Toge Mine, and mining operations only at the Tono Mine. The distribution of radium in waterways has been periodically monitored at fixed monitoring points in mine effluents, river water, river sediments or soil as a link in the chain of the PNC's environmental monitoring programme around the uranium mine. The radium concentration in the waterways has been monitored since 1967 at the Ningyo-Toge Mine and since 1971 at the Tono Mine. The results of environmental monitoring so far indicate that no impact can be found in the vicinity of the mine.

The same programme of environmental surveillance is to be continued in order to watch the trend of radium distribution from the uranium mine.

9.2.7. South Africa

In South Africa, uranium occurs in varying concentrations together with the gold in South African gold mines. Consequently, radium is present in the very large mine dumps which are exposed to the severe environmental conditions pertaining on the Highveld. These lead to leaching, distribution by water and wind, re-precipitation and uptake in streams and aquifers. Human exposure may result through a variety of pathways and a careful analysis is necessary to determine which are critical.

Because these mines have been in operation for many decades before the discovery and extraction of uranium, the environmental survey of radium in the various components of this stable situation, should provide important scientific data which may also be applied to newer and more isolated uranium producers, e.g. at Phalaborwa.

This project was aimed at studying this rather unique situation, which is also of considerable practical importance in view of the increasing number as well as extent of uranium mining and processing activities in South Africa.

9.2.8. United States of America

In the United States of America, the Environmental Protection Agency had assessed the impact of waste discharges from uranium mining and milling on surface and ground waters of the Grants Mineral Belt near Grants, New Mexico. In proximity to the mines and mills shallow ground-water contamination resulted from the infiltration of effluents from mill tailings ponds and mine drainage water. This study in addition to previous EPA studies of inactive uranium mill tailings sites has prompted a programme to evaluate the environmental radiation impact from active uranium mining and milling activities. This information is of great value in assessing the consequences of radium releases to water and help setting the discharge limits. The Environmental Protection Agency has recently proposed regulations to limit radioactivity in the United States drinking water supplies. The proposed maximum level for radium is 5 picocuries per litre of water.

9.2.9. Yugoslavia

In Yugoslavia, the programme was designed:

1) to obtain information about natural radioactivity in surface and drinking waters;
2) to evaluate the population dose from uptake of radium through drinking water;
3) to determine the changes in the environment due to uranium mining and milling effluents.

9.3. ORGANIZATION OF THE PROGRAMME

In order to promote transfer of knowledge and to stimulate interchange and cooperation between participants, the organization included at each meeting discussion and follow-up of studies that were under way or in preparation.

The first goal of the programme was to select and to standardize methods for the determination of radium in water. Two intercomparison runs took place and there was good agreement between laboratories (see chapter 2, section 2.3).

The second aim of the programme was to publish a report, the motive of which evolved in the course of the successive Research Coordination Meetings until the present document was arrived at.

9.4. PROGRESS OF THE PROGRAMME

9.4.1. First Research Coordination Meeting

The initial year was October 1975 and it was intended to hold the first research coordination meeting soon after the commencement of the programme in order to select and standardize the methods of analysis to be used. This meeting was held in spring 1976, in France (Nantes), sixteen participants from six countries attended this meeting, and the Scientific Secretary was Mr. Bonhote. It is worth recalling that the Scientific Secretary indicated that the aim of the project was to publish a report summarizing and discussing the results achieved in the light of environmental and public health protection. The participants agreed that such a report was necessary and a draft outline of chapter headings for such a report, together with an indication of which countries were working in each area, was prepared at that time.

9.4.2. Second Research Coordination Meeting

The second coordination meeting was held at the invitation of the Japanese Government in Yonago City, in October 1977. Participants from eight countries attended this meeting, of which Mr. Farges was the Scientific Secretary; they had the opportunity to visit the very efficient purification plant of the main uranium mine in Japan (Ningyo Toge). During the sessions of the meeting, papers were presented on research performed during the past year, and again the idea of presenting all the data in a booklet at the end of the programme, seemed very attractive to the participants.

9.4.3. Third Research Coordination Meeting

The third coordination meeting was held in Las Vegas and Albuquerque, in October 1978, and a scientific visit was organized to uranium mines and mills in the Grants Belt. According to Mr. Farges, the Scientific Secretary, this meeting was very productive and a gratifying exchange of information took place.

In the Agency Coordinated Research Programmes, a formal review is made by the Committee for Contractual Scientific Services (CCSS) of each coordinated programme, at three-year intervals, in order to ensure that reasonable progress is being made towards the programme goals and that the goals themselves remain valid in relation to the Agency's overall programme. The evaluation prepared in this connection by Mr. Farges, Project Officer, authorized the progress to date (March 1979):

- The first goal of the programme had been reached in selecting and standardizing methods for the determination of radium in water. All the laboratories were using the emanation method with some variants. Two intercomparison runs had taken place and there was now good agreement between laboratories;
- The study on distribution of soluble and insoluble radium was progressing, but some more problems had to be clarified;
- Leaching rates from ore heaps and tailings piles had been investigated, but no major study had been completed;
- The uptake of radium by biological systems had been extensively studied and many results corresponding to various climatic and geological conditions were available;
- Studies of the economic feasibility of radium removal facilities had shown the interest of economic data for possible cost-benefit analysis.

Mr. Farges's evaluation also depicted the programme to be carried out during 2 additional years (1980-81):

- Finalization of the statistical analysis on intercomparison of ^{226}Ra;
- Study of the chemical form and adsorption behaviour of radium in aqueous solutions containing sulfates;
- Study of radium fixation in process effluents;
- Continuation of the investigation of the significance of sediment in the migration of radium in aquatic environments;
- Monitoring of radium in particularly interesting areas: Czechoslovakian and South African mines;

- Ecological studies of radium in various climatic conditions;
- Issue of a booklet entitled "Behaviour of radium in aquifers and waterways".

9.4.4. Fourth Research Coordination Meeting

The fourth and last coordination meeting, of which R. Kirchmann was the Scientific Secretary, was held in Vienna in June 1980.
The first part of the scientific sessions dealt with the findings of the various laboratories during the past twelve months.
The second part was devoted to the preparation of the final draft report.

The future of this coordinated research programme was discussed and the proposals from the participants helped to define the scientific scope and the proposed "new" programme goals.

During the three previous coordination meetings, a technical visit had each time been organized for the participants, so a visit to the Seibersdorf Laboratories seemed appropriate, as the Agency's Laboratory had provided, about two years before, the radium solution standard to the participating laboratories. As the Agency's laboratory is located in the Austrian Research Center, Mr. Hefner, Head of the Health Physics Department, kindly arranged a visit to some of the Austrian laboratories.

9.5. RECOMMENDATIONS

Recommendations from this coordinated research programme were formulated, the main points being:

(a) Field studies and experiments on the leaching and seepage of Ra from tailings piles should be conducted;
(b) Biological uptake of Ra is often species- and site-specific and so more experimental work should be carried out, particularly with reference to the physico-chemical form of the Ra; in this respect wider use should be made of the methods developed during the previous CRP for distinguishing the various forms of Ra in water;
(c) Effects of revegetation of tailings piles on the migration of radium should be studied where examples are available; and
(d) Environmental models should be more widely used to calculate annual ingestion rates for individuals and for populations.

Future work on these problems should include radionuclides other than Ra-216 such as Th-230, Ra-228, Th-228, Po-210 and chemically toxic materials if they are present.

HISTORY OF RESEARCH CONTRACTS AND AGREEMENTS

Agreement No.	1698/R3/CF
Project Officer:	FARGES L.
Chief Investigator:	KUROKAWA, Y.
Institute:	Power Reactor and Nuclear Fuel Development Corporation. Tokyo, Japan
Title:	Studies on the Distribution of Radium in Surface and Waste Water of the Uranium Mines in Japan
Period of Contract	R3 01/05/96 - 30/04/80 R0 01/02/78 - 31/01/79 R1 15/12/76 - 14/12/77 R0 15/10/75 - 14/10/76

Agreement No.	1699/R4/CF
Project Officer:	KIRCHMANN, R.
Chief Investigator:	ZETTWOOG, P.
Institute:	Commissariat a l'Energie Atomique, Fontenay-aux-Roses, France
Title:	Contamination of the Environment by Radium from Tailing Piles of Uranium Mineral Processing Factories
Period of Contract:	R4 01/06/80 - 01/05/79 R3 01/05/79 - 30/04/80 R2 01/03/78 - 28/02/79 R1 01/02/77 - 30/01/78 R0 15/10/75 - 14/10/76

Contract No.	1700/R3/RB
Project Officer:	FARGES, L.
Chief Investigator:	KOBAL, I.
Institute:	Josef Stefan Institute, Ljubljana, Yugoslavia
Title:	Determination of Ra-226 in Surface and Drinking Water
Period of Contract:	R3 15/05/79 - 14/05/80 R2 15/04/78 - 15/04/79 R1 01/12/76 - 30/11/77 R0 01/12/75 - 30/11/76

Contract No.	1729/R3/RB
Project Officer:	FARGES, L.
Chief Investigator:	SEBESTA, F.
Institute:	Faculty of Nuclear Science and Physical Engineering, Technical University of Prague, Prague, Czechoslovakia
Title:	Research Within the Framework of A Coordinated Programme on Studies on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers
Period of Contract:	R3 15/05/79 - 14/05/80 R2 15/12/77 - 14/12/78 R1 15/12/76 - 14/12/77 R0 15/12/75 - 14/12/76

Agreement No. 1769/R3/CF
Project Officer: KIRCHMANN, R.
Chief Investigator: WILLIAMS, A.
Institute: Australian Atomic Energy Commission, Research Establishment, Lucas Heights, Sutherland, N.S.W., Australia
Title: The Movement of Radium in the Sub-Coastal Plains of Northern Australia
Period of Contract: R3 01/02/80 - 31/01/81
R2 01/07/78 - 30/06/79
R1 01/06/77 - 31/05/78
R0 01/04/76 - 31/03/77

Contract No. 1788/R2/RB
Project Officer: FARGES, L.
Chief Investigator: IYENGAR, M.
Institute: Bhabha Atomic Research Centre, Trombay, Bombay, India
Title: Radium in Natural and Processing Areas and its Impact on Human Environment
Period of Contract: R2 01/07/79 - 30/06/80
R1 01/07/77 - 30/06/78
R0 01/04/76 - 31/03/77

Agreement No. 1864/R2/CF
Project Officer: RICHTER, D.
Chief Investigator: SILHANEK, J.
Institute: Office of Radiation Programs, US Environmental Protection Agency, Washington, D.C., U.S.A.
Title: Research within the framework of a Coordinated Programme on Studies on the Source, Distribution, Movement and Deposition of Radium in Inland Waterways and Aquifers
Period of Contract: R2 16/06/79 - 15/06/80
R1 15/04/78 - 14/04/79
R0 01/11/76 - 31/10/77

Contract No. 1865/R2/RB
Project Officer: FARGES, L.
Chief Investigator: PASCHOA, A.
Institute: Pontificia Universidade Catolica, Departamanto de Fisica, Rio de Janeiro, Brazil
Title: Study of Ra-226 Wastes From Uranium mining and Milling Operations
Period of Contract: R2 01/05/79 - 30/04/80
R1 01/12/77 - 30/11/78
R0 01/11/76 - 31/10/77

Agreement No. 2295/R1/CF
Project Officer: KIRCHMANN, R.
Chief Investigator: BASSON, J.
Institute: Atomic Energy Board, Pretoria, South Africa
Title: Movement of Radium from South African Gold/Uranium Mine Dumps into the Aqueous Environment
Period of Contract: R1 01/02/80 - 31/01/81
R0 01/12/78 - 30/11/79

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