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The Environmental Behaviour of Radium: Revised Edition

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THE ENVIRONMENTAL BEHAVIOUR OF RADIUM: REVISED EDITION

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THE ENVIRONMENTAL BEHAVIOUR OF RADIUM: REVISED EDITION

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FOREWORD

A number of industrial activities produce residues containing either uranium or thorium series radionuclides or both. These include the mining and milling of uranium and of other metalliferous and non-metallic ores; the production of coal, oil and gas; the extraction and purification of water; and the production of industrial minerals such as phosphates. Residues from such activities have become of increasing interest from a radiological impact assessment point of view in recent years and isotopes of radium are often of particular interest in such assessments.

The IAEA attaches high importance to the dissemination of information that can assist Member States with the implementation and improvement of activities related to radiation safety standards, including management of radioactive residues containing natural radionuclides, such as radium isotopes.

In 1990, the IAEA published Technical Reports Series No. 310 (TRS 310), The Environmental Behaviour of Radium. Since the publication of TRS 310, a considerable number of publications related to the environmental behaviour of radium have appeared in the literature. It was therefore considered timely to produce a replacement report providing up to date information on key transfer processes, concepts and models that are important in radiological assessments and environmental applications of radium.

This report outlines radium behaviour in terrestrial, freshwater and marine environments. The primary objective of the report is to provide IAEA Member States with information for use in the radiological assessment of accidental releases and routine discharges of radium in the environment, and in remediation planning for areas contaminated by radium. Additionally, applications of radium isotopes as tracers of environmental processes are discussed.

The IAEA wishes to express its gratitude to P. Martin (Australia) for his assistance in editing this report, as well as to those experts who contributed to its development and completion.

The IAEA officers responsible for this report were S. Fesenko, H. Nies and M. Phaneuf of the IAEA Environment Laboratories, in collaboration with G. Proehl of the Division of Radiation, Transport and Waste Safety.

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

The mining and milling of uranium ores produce residues which must be managed safely, including wastewater, tailings and waste rock stockpiles. A number of other industries also produce residues which contain uranium or thorium series radionuclides or both. Examples include phosphogypsum from the phosphate industry and residues from mineral sands processing and from the oil, gas and coal industries. All of these residues are naturally occurring radioactive materials (NORM), for which radiological impact assessments have increasingly been conducted in recent years.

Radionuclides of concern found in NORM mainly include isotopes of U, Th, Ra, Rn, Pb and Po [1.1]. Of these, Ra is of particular importance owing to the presence of Ra isotopes in all three natural decay series, the relatively long half-lives and short lived progeny of two of the isotopes (^{226}Ra and ^{228}Ra), the high mobility of Ra in the environment under a number of common environmental conditions and the tendency of Ra to accumulate in bone following uptake into the body.

Radium was first identified as an important stressor for humans and the environment mobilized by uranium mining and processing industries in the early 1950s [1.2–1.8]. Significant Ra contamination has been identified in many places, arising mainly from uranium, phosphate and even gold mining and milling operations, and from coal ash. Radium isotopes are also important sources of exposure in the oil, gas and coal industry. Additionally, a number of historical industrial sites have been left contaminated with residues from activities involving Ra. Such sites include factories where Ra was used in luminescent paint and Th was used in Th coated gas mantles. Residual contamination is also present at many military establishments and scrapyards [1.9].

In response to the need of its Member States, the IAEA has long supported efforts to develop reports on the environmental fate of Ra. In 1990, it published the IAEA Technical Reports Series No. 310 (TRS 310), which compiled information for the estimation of the impact of Ra on humans and on terrestrial, freshwater and marine environments [1.10].

TRS 310 discussed natural and technologically enhanced sources of Ra, its properties and environmental behaviour as well as methods of analysis in environmental samples, control of releases and assessment of exposure to Ra. Although the main emphasis in the report was on environmental problems caused by uranium mining and milling, it also provided a basis for environmental impact assessments for many contamination scenarios.

It is essential that the information base used for radiological assessments and subsequent remediation planning is kept up to date and this, in itself, is a strong argument for regular revisions of reference documents such as TRS 310. Since its publication, a large number of publications on Ra transfer in the environment have been produced and merit consideration. In particular, in 2004, 2009 and 2010, the IAEA issued a set of basic reports on radionuclide transfers in terrestrial, freshwater and marine environments [1.8, 1.11–1.13]. These reports provided information on key transfer processes, concepts and models that are important in radiological assessments for all radionuclides, including Ra.

Additionally, throughout most of the period from 1991 to the present, the IAEA has run a series of projects aimed at improving environmental assessment and remediation. Through these projects, the environmental behaviour of Ra was considered in many other IAEA reports, mainly in the context of contaminated site characterization and environmental remediation. The topics of these reports include: the characterization of contaminated sites [1.14, 1.15], technical and non-technical factors relevant for the selection of the preferred remediation strategy and technology [1.6, 1.16], an overview of applicable technologies for environmental remediation [1.17], options for the cleanup of contaminated groundwater [1.7], and planning and management issues [1.18–1.21]. In addition, a number of other IAEA publications dealing with related aspects have been compiled as part of various IAEA projects. These include reports on the remediation of uranium mill tailings [1.22] and dispersed contamination [1.23], the decontamination of buildings and roads, the characterization of decommissioned sites and management of radioactive waste and radiation protection in the oil and gas industries [1.8].

Historically, interest in Ra has focused on three aspects, namely its: (a) impact on human health through radiation exposure, (b) application as a tracer of environmental processes and (c) use in various industrial, medical and other applications. This report addresses the environmental behaviour of Ra and so discusses the first two of these aspects but not industrial, medical or other applications. The primary intention of the present report is to support environmental assessments and remediation in areas contaminated by Ra by presenting state of the art concepts, models and parameters rather than providing a summary of all available information on the environmental behaviour of Ra.

There are four Ra isotopes naturally present in the environment: ^{226}Ra of the uranium decay series, ^{228}Ra and ^{224}Ra of the thorium decay series and ^{223}Ra of the actinium decay series. Of these, ^{226}Ra and ^{228}Ra have relatively long half-lives (1600 and 5.75 years, respectively), and the majority of the published literature on Ra relates to these two isotopes. However, both ^{223}Ra and ^{224}Ra, which have half-lives of some days, have several applications, particularly as environmental tracers. As all Ra isotopes exhibit similar behaviour in the environment, the study of one isotope may provide useful information on the behaviour of the other isotopes. Therefore, this report discusses the environmental behaviour of all four naturally occurring isotopes.

The radiological impact of Ra is due to exposure to the Ra isotopes themselves and also to exposure to their decay progeny. In particular, exhalation of the ^{226}Ra decay product ^{222}Rn and of the ^{224}Ra decay product ^{220}Rn from soil, building materials and NORM can result in a significant inhalation hazard. However, this report is focused exclusively on Ra, and does not discuss in detail Ra decay products (such as ^{222}Rn and ^{220}Rn) which may contribute to its total environmental impact.

1.2. OBJECTIVE

This report is primarily intended to provide IAEA Member States with information for use in the radiological assessment of accidental releases and routine discharges of Ra in the environment. The information will ideally also serve as a basis for remediation planning and identification of optimal remediation strategies in areas contaminated by Ra.

1.3. SCOPE

This report covers Ra behaviour in the terrestrial, freshwater and marine environments. The information presented is relevant to the transfer of radionuclides through food chains to both humans and other organisms. The corresponding remedial options and regulatory aspects are also within the scope of this report. Additionally, applications of Ra isotopes to environmental issues are discussed to alert readers to studies that use Ra isotopes as tracers of environmental processes. The report is also intended to be used in conjunction with IAEA reports related to the assessment of the radiological impact of radioactive discharges, as described in Safety Reports Series No. 19, Generic Models for Use in Assessing the Impact of Discharges of Radioactive Substances to the Environment [1.24], IAEA Safety Standards Series No. WS-G-2.3, Regulatory Control of Radioactive Discharges to the Environment [1.18] and other related reports.

1.4. STRUCTURE

This report includes seven chapters. The physical, chemical and biological properties of Ra are discussed in Chapter 2. Chapter 3 addresses sources and presence of Ra in the environment whilst Chapter 4 considers environmental pathways specific to Ra and corresponding models. Dose assessment models related to the occurrence of Ra in the environment and remediation technologies for Ra are given in Chapter 5 and 6, respectively. Chapter 7 presents various case studies describing the main features of environmental impact assessments specific to different contamination scenarios.

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CHAPTER 2

PROPERTIES OF RADIUM

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2.1. A SHORT HISTORY OF RADIUM

Radium was one of the first elements discovered by means of its radioactive properties, and thus was closely linked to the discovery of radioactivity. After the discovery of X rays by Wilhelm Conrad Röntgen in 1895, Henri Becquerel found that uranium salts continuously emit special rays which differ from ordinary light. The origins of the radiation could not be traced to any known sources of energy. This property of matter consisting of the emission of rays was called radioactivity. Subsequently, research by Pierre and Marie Curie showed that radioactivity is high in both U and Th, but that this was their only common characteristic. Additionally, several minerals had stronger radioactivity than the oxides of Th and U and the Curies concluded that these minerals contained some new element with an atomic radioactivity which was much stronger than that of U and Th and which might be present in the minerals in only a very small proportion. This particular hypothesis was verified by their discovery of Po and Ra from pitchblende ore in 1898. The town then known as St. Joachimstal in Bohemia (now Jáchymov in the Czech Republic) was the source of the enormous amounts of pitchblende ore necessary for Pierre and Marie Curie and co-worker Gustave Bémont to extract ^{226}Ra in a measurable quantity [2.1].

In 1903, Becquerel was awarded the Nobel Prize for Physics jointly with Pierre and Marie Curie. Becquerel's citation from the Nobel Committee stated "In recognition of the extraordinary services he has rendered by his discovery of spontaneous radioactivity". The citation for the Curies stated "In recognition of the extraordinary services they have rendered by their joint researches on the radiation phenomenon discovered by Professor Henri Becquerel" [2.2].

Potential uses of U and Ra as sources of radiation for medical, scientific and industrial purposes started being developed shortly after the discovery of the elements. The first Ra refining companies started operation in France as early as 1898 [2.3].

Radioluminescent paint was invented in the early 1900s and originally contained ^{226}Ra. The toxicity of Ra was not initially understood, and Ra based paint saw widespread use, from watches and aircraft instruments to house numbers and doll eyes. During the 1920s and 1930s, the harmful effects of this paint became increasingly clear. A notorious case involved the 'Radium Girls', a group of women who painted watch faces and later suffered adverse health effects from ingestion, through the practice of using their mouth to shape the bristles of the paintbrush into a point. In the second half of the twentieth century, Ra was progressively replaced by safer radionuclides such as promethium147 and, later, tritium. Because it is now recognized that Ra paint requires great care in application, maintenance and disposal to avoid the creation of hazards, consumer products such as clocks and watches increasingly use phosphorescent rather than radioluminescent substances.

At the end of the nineteenth century and into the first few decades of the twentieth century, some people considered that Ra could cure virtually every illness; there was a wide spectrum of conditions for which Ra cures were claimed, including migraine, arteriosclerosis and appendicitis.

In 1913, the Standard Chemical Company of Pittsburgh, whose subsidiary was the Radium Chemical Company, followed the example of the industrialist Armet de Lisle in Paris and opened a medical clinic and laboratory which was advertised as "the first free radium clinic in America". Patients at the clinic were promised no fewer than 30 hours in the Emanatorium and 30 litres of radioactive water to drink. Diseases treated included arthritis, gout, neuritis, diabetes, neurasthenia and pyorrhea. The clinic also claimed that intravenous injection of ^{226}Ra chloride led to a decrease in blood pressure [2.3].

In some instances, the only Ra in the supposedly curative product was in the name (e.g. Ra razor blades or cigarettes) but Ra was found in small amounts in products such as face creams (e.g. Tho-Radia) and liquids intended to be consumed (e.g. Radithor). Radithor marked the end of the so-called mild radiation therapy era, precipitated by the death of Eben Byers, an American millionaire iron and steel industrialist who drank between 1000 and 1500 bottles of Radithor within four years. He developed severe Ra poisoning, including necrosis of the jaw and face, and died in 1932, shortly after the Federal Trade Commission started investigating Radithor [2.3].

More scientifically sound medical treatments involving Ra also began early. The first documented Ra cure of skin cancer was recorded in St. Petersburg in 1903 [2.3]. Over time, different delivery systems were developed to treat various illnesses. These systems can be separated into two main branches: brachytherapy and teletherapy. Radium-226 brachytherapy includes surface applications, e.g. for the treatment of skin cancer; intracavitary applications using gold tubes filled with ^{226}Ra tubes, e.g. for the treatment of cancer of the cervix or uterus; and interstitial applications using ^{226}Ra needles, e.g. for the treatment of cancer of the tongue. Over time, the internally applied devices leak mild amounts of radiation that locally poison the cancer stricken areas of the body, after which the devices are removed from the body. However, Ra is no longer the preferred radionuclide of choice for conducting these procedures and is being replaced by other radionuclides such as iridium or caesium, which have relatively shorter half-lives and lower energies and therefore, the radiation from these isotopes can be more easily shielded. Radium-226 teletherapy is a procedure where the ^{226}Ra source is placed within a machine and used to treat cancer with the source at a distance from the patient. Radium sources were later replaced by cobalt-60, and the first cancer patient was treated by a cobalt teletherapy machine in October 1951 in Canada [2.3].

Today, Ra has only limited applications in research laboratories, for example for the preparation of radon standard solutions, and in Ra-Be neutron sources.

2.2. PHYSICAL PROPERTIES

2.2.1. Isotopes of Ra

There are no stable isotopes of Ra. There are four naturally occurring radioactive isotopes present in the environment because they are part of decay series of primordial radionuclides (Table 2.1 [2.4]).

As shown in Fig. 2.1, ^{226}Ra is part of the ^{238}U series, ^{223}Ra is part of the ^{235}U series and ^{224}Ra and ^{228}Ra are part of the ^{232}Th series. The only anthropogenic isotope with a significant half-life is ^{225}Ra ($t_{1/2}$ = 14.9 d) from the ^{237}Np series, where the immediate parent is ^{229}Th ($t_{1/2}$= 7880 a). This Ra isotope has been used as a yield tracer for Ra chemistry and as the subject of nuclear physics studies, but has not been reported in the environment.

TABLE 2.1. RADIUM DECAY

Isotope	Half-life	Decay constant	Decay mode and energy, MeV	Specific activity Bq/g
^{223}Ra	11.43 (5) d	22.15 a^{-1}	α_3 5.745 (9.1%) α_4 5.714 (53.7%) α_5 5.605 (26.0%) α_6 5.538 (9.1%)	1.896×10^{15}
^{224}Ra	3.632 (2) d	69.7 a^{-1}	α_0 5.685 (94.9%) α_1 5.449 (5.1%)	5.92×10^{15}
^{226}Ra	1600 (7) a	4.33×10^{-4} a^{-1}	α_0 4.784 (94.55%) α_1 4.601 (5.45%)	3.66
^{228}Ra	5.75 (3) a	0.12 a^{-1}	β^-0.046	1.0×10^{13}

2.2.2. Decay series

Each decay series includes a number of isotopes that have a wide range of half-lives and represent a number of elements that have substantially different characteristics. The concentration of each isotope is controlled by that of the parent and the amount of time since fractionation between the isotope and its parent has occurred. For samples sealed over long timescales, the activity of each isotope (the decay rate) is the same as that of its parent, i.e. it is in secular equilibrium with its parent. For example, for the ^{232}Th decay series,

$$(^{232}Th) = (^{228}Ra) = (^{228}Th) = (^{224}Ra) = \ldots \tag{2.1}$$

following a standard notation where an isotope in parentheses, e.g. (^{232}Th), denotes the activity of that isotope. There are two important points to note:

(a) In secular equilibrium, the distribution of a daughter isotope is controlled by that of the parent isotope, and so ultimately all isotopes in the series are controlled by the long lived parent (here, ^{232}Th);

(b) While the activities are equal, the molar abundances are inversely proportional to the decay constants, so that the concentrations of very short lived nuclides are very low.

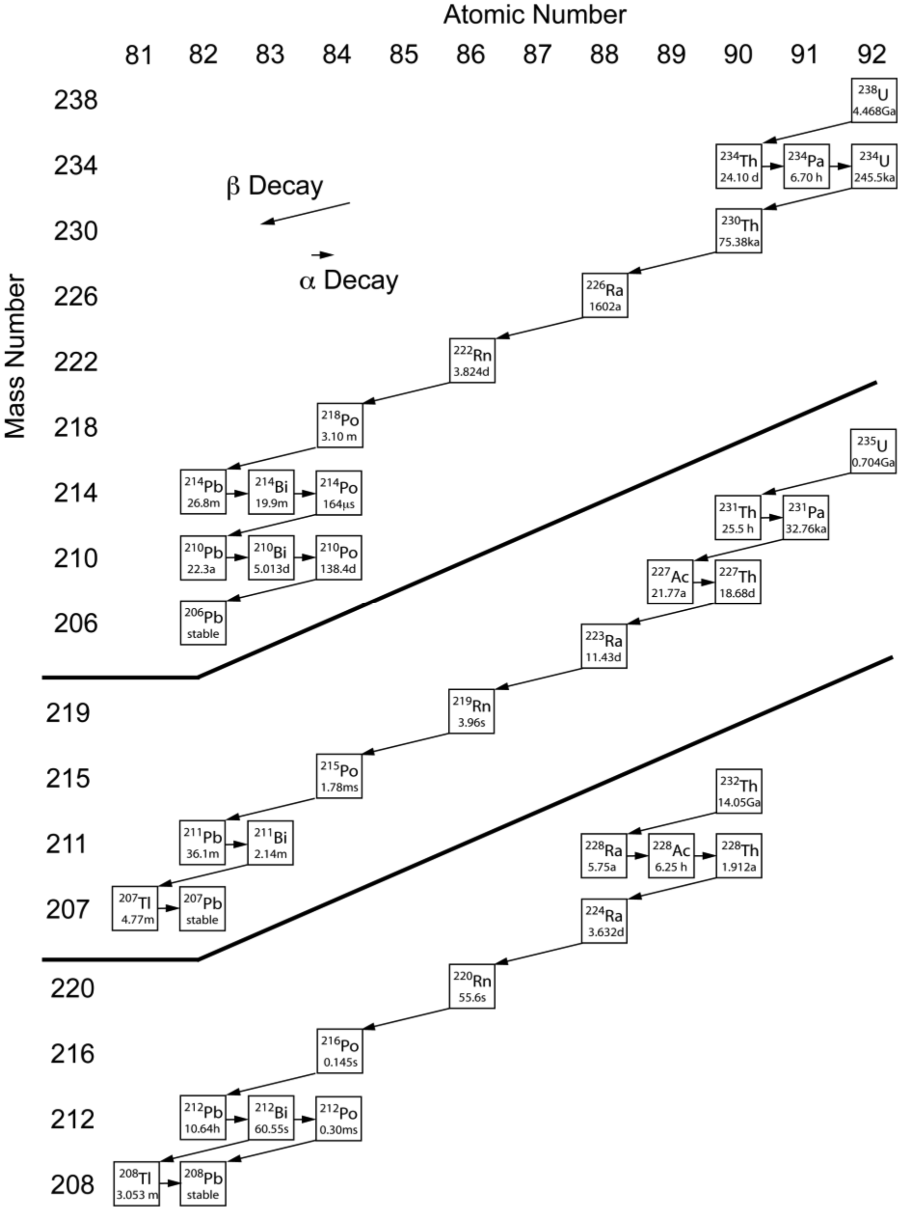

FIG. 2.1. Decay series.

For the ^{232}Th decay series, the molar ratio at secular equilibrium is:

$$\frac{^{228}\mathrm{Ra}}{^{232}\mathrm{Th}} = \frac{\lambda_{232\mathrm{Th}}}{\lambda_{228\mathrm{Ra}}} = \frac{^{228\mathrm{Ra}}t_{1/2}}{^{232\mathrm{Th}}t_{1/2}} = 4.0 \times 10^{-9} \tag{2.2}$$

and

$$\frac{^{224}\mathrm{Ra}}{^{232}\mathrm{Th}} = \frac{^{224\mathrm{Ra}}t_{1/2}}{^{232\mathrm{Th}}t_{1/2}} = 7.1 \times 10^{-13} \tag{2.3}$$

For the ^{238}U decay series, the molar ratio is:

$$\frac{^{226}\mathrm{Ra}}{^{238}\mathrm{U}} = \frac{^{226\mathrm{Ra}}t_{1/2}}{^{238\mathrm{U}}t_{1/2}} = 3.6 \times 10^{-7} \tag{2.4}$$

For the ^{235}U series:

$$\frac{^{223}\mathrm{Ra}}{^{235}\mathrm{U}} = \frac{^{223\mathrm{Ra}}t_{1/2}}{^{235\mathrm{U}}t_{1/2}} = 3.1 \times 10^{-8} \tag{2.5}$$

For all natural U:

$$\frac{^{238}\mathrm{U}}{^{235}\mathrm{U}} = 137.88 \qquad \text{and so:} \quad \frac{(^{238}\mathrm{U})}{(^{235}\mathrm{U})} = 21.8 \tag{2.6}$$

While there is some variation in the Th/U ratio in rocks and soils, for the continental crust the average ratio is:

$$\frac{^{232}\mathrm{Th}}{^{238}\mathrm{U}} = 3.8 \qquad \text{and so:} \quad \frac{(^{232}\mathrm{Th})}{(^{238}\mathrm{U})} = 1.2 \tag{2.7}$$

Therefore, even where U and Th are strongly enriched, Ra isotopes have extremely low molar concentrations. Clearly, Ra is composed predominantly of ^{226}Ra, although Ra activity concentrations due to ^{224}Ra and ^{228}Ra are comparable. ^{223}Ra is a minor constituent, but an important tracer in the marine environment.

Each Ra isotope is generated from the decay of a corresponding Th isotope (Fig. 2.1). When a physical or chemical process separates Ra from its parent Th isotope, the radioactivity of the daughter Ra isotope will evolve towards that of the parent until they are once again equal to one another. As shown in Fig. 2.2, the daughter isotope activity will change at a rate according to its half-life, and the difference between the parent and daughter activities will be halved after each half-life. This will occur for each isotope in a decay series, so that the activity of each parent Th isotope may also change at the same time to reach the activity of its parent. Where Ra is completely isolated from its parent, it will simply decay away.

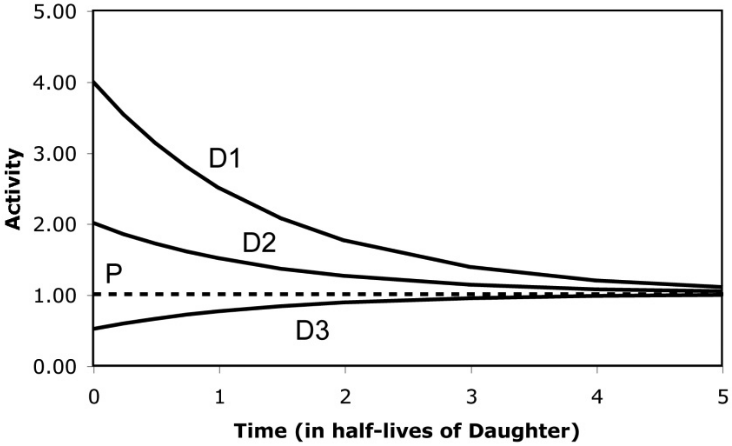

FIG. 2.2. Daughter isotope activity over time.

2.3. RADIUM DECAY PRODUCTS

Each Ra isotope produces a chain of daughters that are very short lived and contribute to the overall radiation load of a Ra bearing substance. For ^{223}Ra and ^{224}Ra, the daughter isotopes all have very short half-lives (Table 2.2 [2.4]), and so will rapidly grow into secular equilibrium with the parent Ra isotope as described above. For ^{226}Ra, the immediate decay product is the noble gas ^{222}Rn, which may be readily lost prior to decay from non-retentive materials. However, in minerals or large organisms, the ^{222}Rn may not escape before decay, and so will generate a chain of short lived daughter nuclides. If the ^{210}Pb has been recently separated from ^{226}Ra, then this isotope will accumulate over the timescale of its half-life (22.3 a). Similarly, while the activity of ^{210}Bi will follow that of ^{210}Pb, the isotope ^{210}Po will slowly grow into secular equilibrium with ^{210}Pb as determined by its half-life of 138 d. For ^{228}Ra, the immediate daughter ^{228}Ac will generally be found in secular equilibrium with its parent, while the activity of ^{228}Th will grow into secular equilibrium with ^{228}Ra according to its half-life of 1.9 a.

TABLE 2.2. RADIUM DAUGHTERS AND DECAY ENERGIES

Isotope	Half-life	Decay mode	Decay Energy keV
^{223}Ra	11.43 d	α	5979
^{219}Rn	3.96 s	α	6946
^{215}Po	1.78 ms	α	7526
^{211}Pb	36.1 min	β^-	1367
^{211}Bi	2.14 min	α	6750
^{207}Tl	4.77 min	β^-	1418
^{207}Pb	Stable	—	—
^{224}Ra	3.66 d	α	5789
^{220}Rn	56 s	α	6405
^{216}Po	0.15 s	α	6906
^{212}Pb	10.6 h	β^-	569.9
^{212}Bi	60.6 min	β^- 64.1% α 35.9%	2252 6207
^{212}Po	0.4 µs	α	8954
^{208}Pb	Stable	—	—
^{226}Ra	1600 a	α	4871
^{222}Rn	3.8 d	α	5590
^{218}Po	3.05 min	α	6115
^{214}Pb	26.8 min	β^-	1019
^{214}Bi	19.8 min	β^-	3270
^{214}Po	162 µs	α	7833

TABLE 2.2. RADIUM DAUGHTERS AND DECAY ENERGIES (cont.)

Isotope	Half-life	Decay mode	Decay Energy keV
^{210}Pb	22 a	β^-	63.49
^{210}Bi	5.0 min	β^-	1161
^{210}Po	138 d	α	5047
^{206}Pb	Stable	—	—
^{228}Ra	5.75 a	β^-	45.81
^{228}Ac	6.13 h	β^-	2124
^{228}Th	1.9 a	α	5520
^{224}Ra	3.66 d	α	5789
^{220}Rn	56 s	α	6405
^{216}Po	0.15 s	α	6906
^{212}Pb	10.6 h	β^-	569.9
^{212}Bi	60.6 min	β^- 64.1% α 35.9%	2252 6207
^{212}Po	0.4 µs	α	8954
^{208}Pb	Stable	—	—

— = no data available

The short lived nuclides further along the decay chain may have activities equal to that of ^{228}Th, depending on the environmental medium. Overall, the impact of the ^{226}Ra and ^{228}Ra daughters will depend upon the retention of ^{222}Rn and the time of separation from ^{210}Pb, ^{210}Po and ^{228}Th.

2.4. CHEMICAL PROPERTIES

2.4.1. Basic characteristics

Radium is an alkaline earth metal, with atomic number Z = 88. It is expected to have similar chemical characteristics to those of the other alkaline earths (Table 2.3), as all these elements are only present in nature in the +2 oxidation state. There are various trends in behaviour across the group due to increasing ionic radius with atomic number. The behaviour of Ra is similar to that of Ba due to the similarity of their ionic radii. Therefore, where Ra data are not available, Ba has often been used as a chemical analogue for predicting Ra behaviour.

Radium can be readily separated through chemical processes from its parent, Th. Thorium is highly insoluble in natural waters, and strongly adsorbs onto mineral surfaces. It has a strong affinity to humic acids and other organic ligands, and so can be concentrated in organic deposits or transported in organic colloids [2.5]. In contrast, U is highly soluble under oxidizing conditions. It is readily adsorbed onto mineral surfaces, though to a lesser degree than Th and Ra, and can be complexed by organic ligands. Uranium is also incorporated into secondary Fe oxyhydroxides, where daughter nuclides can be retained.

TABLE 2.3. ELEMENT CHARACTERISTICS

Element	Atomic number	Crystal ionic radius (Å)	Hydrated ionic radius (Å)	Electronegativity
Sr	38	1.13	4.12	0.99
Ra	88	1.52	3.98	0.90
Mg	12	0.65	4.28	1.23
Ca	20	0.99	4.12	1.04
Ba	56	1.35	4.04	0.97

2.4.2. Aqueous speciation

The aqueous speciation of Ra is reviewed by Dickson [2.6]. Values for the equilibrium constant *K* for the formation of the primary Ra complexes in most natural waters are given in Table 2.4. In low salinity solutions, Ra will be present as uncomplexed Ra^{2+}. Langmuir and Riese [2.7] calculated thermodynamic data for Ra complexes from data from other alkaline earths (see Table 2.4 [2.7, 2.8]). In waters with high sulphate concentrations, a significant fraction of Ra^{2+} would be in the sulphate form; for a sulphate concentration of 70 mg L^{-1}, half of the Ra would be found as $RaSO_4$. In contrast, in water with a Cl concentration as high as a salinity of 4, only 10% would be in the form $RaCl^-$. A significant fraction of Ra would be complexed as $RaCO_3$ only at high pH (>10.25) and high carbonate concentrations (>60 mg/L) [2.8].

TABLE 2.4. AQUEOUS Ra COMPLEXES

Complex	Log *K*	
$Ra^{2+} + OH^- = RaOH^+$	0.5	—
$Ra^{2+} + Cl^- = RaCl^+$	−0.10	—
$Ra^{2+} + CO_3^{2-} = RaCO_3$ (aq)	2.5	2.48
$Ra^{2+} + SO_4^{2-} = RaSO_4$ (aq)	2.75	2.43
$Ra^{2+} + HCO^{3-} = RaHCO_3^+$	—	2.89
Ref.	[2.7]	[2.8]

— = no data available.

2.4.3. Precipitation

Due to the very low molar concentrations of Ra in the environment, precipitation of Ra phases is rarely important. Rather, removal from waters can occur by co-precipitation of phases in which Ra forms a solid solution. Barium is typically present in natural waters [2.9] and groundwaters [2.10] in molar concentrations 10^8 times greater than those of Ra. In the presence of moderate amounts of sulphate, Ba concentrations may be controlled by the precipitation of barite, $BaSO_4$, as typical Ba concentrations are generally near saturation levels. Barite can incorporate Ra in solid solution as $(Ba,Ra)SO_4$. The incorporation of Ra can be described by the empirical partition coefficient determined from the ratio of Ra/Ba measured in the solution compared to that measured in the surface of minerals in contact with the solution:

$$\lambda = \frac{([\mathrm{Ra}]/[\mathrm{Ba}])_{\mathrm{surface}}}{([\mathrm{Ra}]/[\mathrm{Ba}])_{\mathrm{solution}}} \tag{2.8}$$

Values for λ of 1.21 [2.11] to 1.8 [2.12] have been reported. As discussed extensively (e.g. in Refs [2.13, 2.14]), this is an empirical relationship, which may partly reflect kinetic effects and which also deviates from a thermodynamic equilibrium constant calculated from free ion activities. Bosbach et al. [2.14] experimentally investigated how barite can incorporate Ra from solution through recrystallization. Precipitation of $(Ba,Ra)SO_4$ has been shown to be an important process in controlling the solubility of Ra in a range of natural waters [2.6, 2.15–2.21]. Langmuir and Melchior [2.21] found that in some deep brines in north Texas, the concentrations of dissolved Ra were likely controlled by co-precipitation of trace Ra in celestite ($SrSO_4$) as well as barite.

Radium in gypsum ($CaSO_4{\cdot}2H_2O$) was measured by Yoshida et al. [2.22] who found a λ value of 0.32 ± 0.15. This is substantially lower than the value for barite, reflecting the much greater difference in ionic radius between Ra and Ca than between Ra and Ba.

In waters with high carbonate concentrations, the alkali earths can be precipitated as carbonates. Curti [2.13] reviewed available data on incorporation of a wide range of elements and radionuclides into calcite, and preferred the partition data of Tesoriero and Pankow [2.23]. Ba/Ca ratios in precipitated calcite of 0.012 ± 0.05, relative to the dissolved ratio, were taken for Ra. Yoshida et al. [2.24] reported a comparable value of 0.016 ± 0.011 for Ba but a somewhat higher value of 0.15 ± 0.06 for Ra. While Andrews et al. [2.25] suggested that calcite precipitation controls dissolved Ra in the Stripa granite based on a correlation between Ra and Ca, Gnanapragasam and Lewis [2.26] found that the Ra/Ca ratio in precipitated calcites is $\sim 10^{-2}$ times the value for the source solution, and so calcite is unlikely to be a common control on Ra concentrations. Dietzel et al. [2.27] found a substantially higher value for Ba of 1.4 for inorganic aragonite, with significant temperature dependence. More rapidly precipitated carbonate results in higher partition coefficients. Rihs et al. [2.28] found values of 0.47–0.80 for Ra and 0.68–0.96 for Ba precipitated from hydrothermal waters discharged at the surface, while Sturchio [2.29] found 0.33 for Ra and 0.63 for Ba in hydrothermal deposits.

2.4.4. Adsorption and desorption

The concentrations of Ra in waters and the mobility of Ra through the environment are generally controlled by interaction with surfaces by adsorption through ion exchange. This is commonly described by a partition coefficient (K_d), which is defined as:

$$K_d = \frac{\text{concentration in solid phase}}{\text{concentration in solution}} \tag{2.9}$$

The concentration in the solid phase is expressed as the amount of adsorbent in a total mass of solid (in e.g. moles/kg), while the concentration in solution is expressed in moles L^{-1}. Therefore, the unit of K_d is in terms of volume of solution to mass of solids (e.g. L/kg). Data for Ra K_d values are limited compared to many other contaminants. For determining the extent of adsorption at specific sites, the values for natural samples are needed to account for all of the different available surfaces. Nonetheless, values for specific materials from laboratory experiments are useful for evaluating the controlling factors. In addition to concerns that experiments have been performed under applicable conditions and have reached equilibrium, spuriously high values can be obtained due to co-precipitation of Ra with $BaSO_4$. Recent data compilations and discussions of Ra adsorption include Ref. [2.30].

2.4.4.1. General adsorption

The studies reviewed below indicate that Ra is readily adsorbed to clays and mineral oxides present in soils, especially at near neutral and alkaline pH conditions. For the pH conditions of most natural waters, dissolved Ra will be present primarily as the uncomplexed Ra^{2+} cation. Sorption studies generally confirm the adsorption behaviour expected for Ra^{2+} as a function of pH, with negligible adsorption at very acidic pH values and increasing adsorption with increasing pH. As discussed in Ref. [2.31], the pH range at which adsorption of cations begins to increase on mineral surfaces depends on the values of the point of zero charge (PZC) for each type of mineral, when the electrical charge density on a surface is zero. In general, at pH values of less than the PZC, the mineral surface has a net positive charge and strongly adsorbs anions. At pH values greater than the PZC, the surface strongly adsorbs dissolved cations. Radium competes with other alkaline earth cations for sorption sites. In comparison to other alkaline earth elements, the relative affinity of this group of elements for ion exchange is: $Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ [2.32]. The adsorption of Ra has been shown to be strongly dependent on ionic strength and concentrations of other competing ions in that adsorption of Ra decrease with increasing ionic strength. Overall, for widespread phases, Ra is less efficiently sorbed onto iron oxides [2.33] and more efficiently sorbed onto secondary minerals with high cation exchange capacity (CEC) than is U [2.34].

Even for specific materials, adsorption constants are strongly dependent upon solution composition (e.g. Eh, pH and other cations), temperature [2.35], surface characteristics and degree of alteration. The studies discussed below provide a guide to Ra behaviour in the environment, though site specific values will ideally be determined taking into account mineralogy, actual water chemistry and competing ions, mineral chemistry, surface chemistry, availability of active surfaces and variations in site conditions.

Clays. Relative to other alkaline earth elements, Ra is the one most strongly sorbed by ion exchange on clay minerals. Further, clays generally have a high specific surface area due to their fine grained nature. Therefore, in any soils, aquifers or rocks that have been exposed to weathering, these phases have strong effects on Ra migration.

Kaolinite is commonly formed by alteration of aluminosilicate minerals, in particular from feldspars by leaching of Na, Ca and other cations by weathering. It is therefore typically found in granitic rocks, especially those weathered under conditions of relatively low pH. Amongst the common clay groups, kaolinites generally have relatively low CECs (3–15 meq/100 g at pH = 7; [2.32]). Results from Riese [2.36] (see also Langmuir [2.37]) indicate that significant adsorption of Ra occurs on kaolinite over a pH range of 3–9. The adsorption of Ra increases with increasing pH, especially at pH values greater than 6, and decreases with increasing concentrations of dissolved calcium. However, Beneš et al. [2.38] found that adsorption was less than on montmorillonite, and that the pH dependency of Ra adsorption on kaolinite was less than that determined for ferric hydroxide and quartz. For a pH of 7.58, a partition coefficient (K_d) of ~2900 mL/g at low Ra concentrations was found, and generally varied according to a Langmuir isotherm. Ra was easily desorbed by changing solution chemistry, and was strongly affected by competition from other ions. Ames et al. [2.34] conducted batch experiments at different temperatures and a wider concentration range, and found a weak dependence of K_d on temperature and concentration, with a K_d of ~500 mL/g at 25°C and 0.05 Bq/L in solution.

Smectites are widely found in soils and can form very fine grained, mobile material that can be concentrated in depositional depressions and certain soil horizons. These typically have high CECs (70–100 meq/100 g [2.32]). Tachi et al. [2.39] used batch experiments to study the sorption of Ra on bentonite (a mixture of smectite, quartz and minor amounts of other phases) and separated Na smectite. The measured K_d values ranged from 10^2 to $>10^4$ mL/g, and were dependent on ionic strength and pH. Most of the sorbed Ra was readily desorbed by a 1 mol/L KCl solution. Radium sorption on bentonite was dominated by ion exchange with smectite, though there was a dependence on pH due to changes in Ca concentrations caused by dissolution and precipitation of calcite. Beneš et al. [2.38] reported a partition coefficient of ~8700 mL/g for montmorillonite at a pH of 7.47 and low Ra concentrations varying according to a Langmuir isotherm. This value is three times higher than that of kaolinite in the same solution. There was a moderate dependence on pH and a strong dependence on ionic strength, with decreasing Ra adsorption due to competing ions. Adsorption experiments were also performed by Ames et al. [2.34] over a greater range and at different temperatures, and Freundlich isotherms were fitted to the data. They found a value of K_d ~3800 cm^3/g at 25°C and 0.05 Bq/L in solution. Nontronite, a Fe rich smectite formed from the weathering of basalts and biotites, was found to have a much higher K_d (~18,000 cm^3/g).

Illite is a weathering product of micas and feldspar, and is commonly found in soils and sedimentary rocks. These minerals typically have cation exchange capacities of 10–40 meq/100g [2.32], intermediate between kaolinites and smectites. Ames et al. [2.34] found a K_d of ~8500 mL/g at 25°C and 0.05 Bq/L in solution for illite, and ~2000 cm^3/g for Fe rich glauconite, which forms by diagenetic alteration in reducing sediments.

Mineral oxides. Fe and Mn oxyhydroxides are widely distributed alteration products: they have very high CECs, and so high potential for controlling cation migration in the environment.

Fe oxyhydroxides. Radium has been found to adsorb onto oxidized Fe phases that are widely found as weathering products on rock surfaces, in soils and within aquifers. Fe is contained in various primary minerals, and Fe oxyhydroxides form as fine-grained particles and surface coatings. Beneš et al. [2.40] reported that adsorption of Ra onto ferric hydroxide is strongly dependent upon pH, with >50% adsorption occurring above pH ~8, and is readily reversible. Therefore, the extent of adsorption changes substantially within the pH range of natural waters.

Ames et al. [2.41] studied Ra partitioning onto amorphous ferric oxyhydroxide and found that Ra varied along a Freundlich isotherm over a wide concentration range; they determined a value of K_d ~3000 mL/g at 25°C and 0.05 Bq/L in solution.

MnO_2. Manganese oxide is known to strongly scavenge Ra, and is routinely used to concentrate Ra from water samples (see Section 2.5). Manganese oxides commonly occur in sediments as coatings and fine aggregates with large surface areas, and so can be important in controlling Ra behaviour even at low bulk compositions. While many Mn minerals have been reported, Mn oxides are typically fine-grained and poorly crystalline and so often remain uncharacterized [2.42]. The stability of Mn phases is sensitive to water conditions, with the solubilities controlled by redox reactions between soluble Mn(II) and insoluble Mn(III) and Mn(IV), which may link bulk Ra adsorption to changes in pH and Eh. This has been argued for some groundwaters by Sturchio et al. [2.43], and Zukin et al. [2.44]. Koulouris [2.45] investigated the sorption of Ra on MnO_2, and observed no dependency as a function of pH at values greater than 3.6, nor on initial Ra concentrations and chemical species. Manganese oxides also efficiently scavenge Ra from solution in the marine environment.

2.4.4.2. Other common minerals

Beneš et al. [2.19] reported a value for K_d of 9×10^4 mL/g for pH 7.50 from freshly ground muscovite, and so substantially higher than measured in clays. Ames et al. [2.33] also found strong partitioning of Ra onto muscovite with some dependence on temperature, and measurements over a broader concentration range fitting a Freundlich isotherm. Somewhat greater adsorption was found on biotites. Beneš et al. [2.19] also studied Ra adsorption onto albite, and found a K_d of 3×10^4 mL/g for pH 8.05, with adsorption relatively constant above pH 6 but sensitive to the concentration of Na ions. Beneš et al. [2.40] reported experiments on Ra adsorption on quartz. At pH 7.37, the K_d was ~2×10^3 mL/g and the Ra was easily desorbed. Maiti et al. [2.46] found that adsorption of Ra onto calcite, dolomite and anhydrite is minimal, although Th can be strongly adsorbed onto these phases.

2.4.4.3. Organic matter

Only a few studies have been conducted on the adsorption of Ra on organic matter. The results of these studies suggest that Ra may be strongly adsorbed by organic material in soils [2.47–2.49]. Nathwani and Phillips [2.48, 2.49] used batch equilibration experiments to study ^{226}Ra adsorption by soil with different physicochemical characteristics. The measured ^{226}Ra adsorption followed Freundlich adsorption isotherms over a large range of ^{226}Ra concentrations. Organic matter and clay were determined to be the dominant phases contributing to the adsorption of ^{226}Ra on these soils. Nathwani and Phillips [2.48] suggested that adsorption affinity of the organic matter and clays is primarily due to their CEC. Their results also indicated that organic matter adsorbs approximately 10 times more ^{226}Ra than the clays. Greeman et al. [2.47] determined that Ra is enriched in the organic (humic) matter fraction of selective chemical extraction separations of soils.

2.5. DETERMINATION OF RADIUM ISOTOPES

The types of samples for which Ra determinations may be required for various applications are very diverse, and the range of activity concentrations which may be encountered is large. Moreover, there are four naturally occurring isotopes of Ra for which determinations may be required, and for these a number of analytical approaches are possible. Consequently, the topic of determination of Ra isotopes is quite complex. Recently, the IAEA published a comprehensive review of analytical methodology for the determination of Ra isotopes in environmental samples [2.50]. The standard text Methods of Seawater Analysis [2.51] also contains a chapter on the determination of natural radioactive tracers, including Ra [2.52]. Consequently, only a short summary of the main issues on this topic is presented here.

The most commonly applied detection methods for Ra isotopes are gamma spectrometry, alpha spectrometry, liquid scintillation counting (LSC), mass spectrometry and alpha counting of the ingrown Rn daughters. In each case, a source suitable for the detection system must be prepared. For the preparation of the source, several steps are typically required which will include some or all of the following: sample preservation and pretreatment, sample dissolution, Ra preconcentration, separation and purification of Ra from interfering elements and preparation of the final source.

Water samples are generally acidified after collection to prevent adsorption of Ra to the container walls. An exception is seawater samples, which are almost never acidified upon collection. Instead they are generally passed through a column of Mn fibre [2.53] to preconcentrate the Ra from 100 to 1000 L of seawater. The short lived isotopes may be measured immediately by delayed coincidence counting [2.54]. Later, the Mn fibre may be leached, and Ra co-precipitated with $BaSO_4$ and measured by gamma spectrometry [2.55].

Solid materials (e.g. soil, sediment and biota) are usually dried at 80–110°C over 12–48 h and ashed in a temperature range of 450–800°C over a period of 12–48 h to destroy the organic matter which can complex radionuclides to a significant extent. If the analytical technique requires the breaking up of the matrix of solid materials, the samples have to be decomposed by ashing, wet techniques under exposure of various acid combinations or fusion techniques via melting with different salt mixtures. For complete or nearly complete dissolution by wet digestion, strong oxidizing acids at raised temperatures are used, such as concentrated or fuming nitric acid, aqua regia, sulphuric acid or mixtures of concentrated nitric acid with perchloric acid or hydrofluoric acid. To accelerate the wet digestion, the leaching and decomposition can be supported by applying high pressure in an autoclave system [2.56].

A fusion technique with a suitable fluxing base or salt and optional additives is used for the destruction of refractive material. The various procedures derived from developments for analysing the composition of geological samples [2.57] and adjusted to the demands of the radiochemical analyst can involve application of hydroxides [2.58], peroxides [2.59], fluorides, pyrosulphates [2.60], carbonates [2.61] or borates [2.62] as fluxes, alone or in mixtures. The methods are usually very fast, requiring 5–60 min.

The most frequently applied preconcentration method is co-precipitation. Typical methods for Ra separation are co-precipitation, ion exchange chromatography, extraction chromatography (solid phase extraction) and solvent extraction.

Samples of water with a low total quantity of dissolved substances (e.g. potable, mineral, ground or rainwater) can in many cases be preconcentrated by evaporation without any selectivity regarding the enrichment of Ra. In particular, evaporation is a common source preparation method for the determination of Ra by gamma spectrometry.

Co-precipitation is practicable for the preconcentration of analytes from larger water samples and for the separation of the analyte from matrix components and other radionuclides. Co-precipitation with Ba sulphate is the most often employed preconcentration step, and is simultaneously associated with separation and purification. Other specific co-precipitations can be carried out with Ba chromate or oxalate, calcium or aluminium phosphate [2.56] and strontium sulphate [2.63].

Manganese dioxide (MnO_2) freshly precipitated from small volumes of water (up to 10 L) effectively removes a variety of radionuclides (including Ra, Th, U, Po, Ac and Pb) which are assumed to be dissolved [2.52]. Mn fibres [2.54] can be used to preconcentrate Ra isotopes from up to 1000 L of seawater [2.64].

For Ra separation, strong acidic cation exchange resins are frequently used. The samples may be loaded on the column dissolved in dilute acids (HCl or HNO_3), and the less retained components eluted with HCl or HNO_3 of increasing concentrations, with Ra being finally stripped with 4–9 M HCl or 4–5 M HNO_3. By this procedure, Mg and Ca are removed effectively, but the Ra fraction remains contaminated with Ba, Sr [2.65] and lanthanide impurities [2.66]. Frequently used cation exchange resins are BioRad AG50WX8 or Dowex 50WX8. In the 1970s, Gleason [2.67] developed one of the first successful approaches for the separation of Ra and Ba using CyDTA as selective eluent.

The MnO_2 resin consists of an inert macroporous carrier substrate on which the manganese dioxide is precipitated in finely divided form by reduction. For the retention of Ra from deionized and low salinity water, the optimal pH ranges are 4–8, where recoveries of greater than 90% are achieved [2.68]. Recently, a more specific material, the Sr resin, has had widespread application for the removal of Ba and Pb from Ra. Strontium resin is the trade name for an extraction chromatographic (EC) material containing 4,4’(5’)-di-t-butylcyclohexano-18-crown-6 ether as an extractant [2.69]. In 3 M HNO_3 solution, the nitrate complexes of Ba, Sr and Pb are retained with increasing distribution coefficients. Radium is collected in the effluent.

The Radium Rad Disks from 3M are filter like membranes that consist of an inert polymer matrix of polytetrafluoroethylene fibrils in which particles of Ra ion selective organic compound (a crown ether) is embedded [2.70]. The disks are mainly dedicated for the rapid determination of the longer living Ra isotopes

^{226}Ra and ^{228}Ra in environmental water samples or similar aqueous solutions up to a volume of 4 L.

The Ra isotopes ^{226}Ra, ^{223}Ra and ^{224}Ra are alpha particle emitters and can be directly measured by alpha spectrometry. The beta emitting Ra isotope ^{228}Ra can be indirectly measured by alpha spectrometry via its progeny ^{228}Th or ^{224}Ra. However, because of the long half-life of ^{228}Th ($T_{1/2}$ = 1.9 a), the in-growth period ranges between 3 and 18 months (depending on the ^{228}Ra activity and required sensitivity), and hence for routine analysis of ^{228}Ra alpha spectrometry this is not generally a practical measurement method. A prime disadvantage of alpha spectrometry is the necessity for time consuming chemical dissolution and Ra separations on the sample for preparation of the thin source required.

An advantage of alpha spectrometry is the ability to use an internal yield tracer. The most commonly used tracers are ^{223}Ra, ^{224}Ra, ^{225}Ra and ^{133}Ba. The isotope ^{225}Ra is an ideal tracer because it does not occur naturally, and because it may be measured using the 7.07 MeV peak of its progeny ^{217}At [2.71]. The use of ^{223}Ra or ^{224}Ra is only suitable for the determination of ^{226}Ra and ^{228}Ra, and their level in the sample has to be estimated to enable the addition of a quantity large in comparison to the present activity. The determination of ^{223}Ra with ^{224}Ra and vice versa is not practical because the main alpha peaks of both nuclides overlap with each other. The use of the non-isotopic tracer ^{133}Ba exposes some weak points. Although the elements are chemically very similar, the small differences can bring about significant deviations in the recovery of Ra and Ba during the individual working steps [2.72].

Radionuclides other than Ra can be present in the sample matrix and can disturb the alpha spectrometric determination of the Ra nuclides when they are not separated completely. For example, interferences with the alpha energy of ^{226}Ra could be caused by ^{230}Th, ^{229}Th, ^{231}Pa and ^{234}U. Interferences with the alpha energies of ^{223}Ra and ^{224}Ra can occur by $^{243+244}$Cm, ^{241}Am, ^{238}Pu, ^{228}Th, ^{227}Th, ^{225}Ac, ^{222}Rn, ^{218}Po, ^{213}Bi and ^{210}Po. However, because of the preceding chemical separations, the number of radionuclides possibly emerging at the measurement is rather limited, and such interferences are unusual. A more common difficulty arises from the separation of the contributions to various peaks due to the complexity of the Ra alpha spectrum.

An attractive feature of gamma spectrometry is the ability to use bulk samples that often require little or no radiochemical preparation. For solid materials including soils and sediments, the sample can often be directly placed into the sample holder or container after only very basic preparation (e.g. drying, ashing, sieving). Sample homogeneity is also more easily attained with the larger sample sizes typically used. Another strong advantage of gamma spectrometry is the ability to determine ^{224}Ra and also ^{228}Ra by measurement of the gamma rays of its progeny ^{228}Ac). However, sample matrix effects (including self-attenuation) and paired coincidence decays need to be considered when analysing by gamma spectrometry [2.73].

There are two basic approaches to the determination of ^{226}Ra by gamma spectrometry [2.74]. The first is by measurement of the ^{226}Ra peak at 186.2 keV. Unfortunately, the emission probability of this gamma photopeak is quite weak (3.6%), and there is interference from the primary gamma emission of ^{235}U at 185.7 keV, which has a high photon emission probability of 57%. Hence, this approach requires an independent estimate of ^{235}U to allow for this interference [2.75]. An alternative and more sensitive approach is to measure the strong gamma lines of the ^{222}Rn progeny ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV). However, the application of this approach requires an ingrowth period (generally of approximately 3–4 weeks) for ^{222}Rn, and the sample needs to be sealed over this period to prevent the loss of ^{222}Rn to the atmosphere.

LSC for Ra determination can be divided into two general groups: where no sample preparation is required, and, alternatively, where radiochemical methods may be used prior to measurement. Measurements in the first category are performed either without a cocktail (Cerenkov counting), with a water immiscible cocktail (as a two phase sample), or as a homogeneous or semi-homogeneous sample (for ^{226}Ra and ^{228}Ra). Such methods can only be used for samples with relatively high activity, otherwise the counting time needs to be rather long. The second method can be applied not only for the determination of ^{222}Rn but also for the determination of ^{226}Ra in water samples [2.76]. In this method, radon is extracted from the water phase into an organic phase (containing the scintillation cocktail, leaving Ra and other interfering radionuclides in the aqueous phase). A method of direct Ra determination is a simple mixing of the water sample with a water miscible cocktail. In this method, the cocktail forms a homogeneous mixture with the sample [2.77]. The interference of other radionuclides is, however, a limiting factor for the determination of Ra isotopes. Co-precipitation with a Ba carrier is the most popular technique for Ra preconcentration and purification for LSC applications, as the sample volume can be reduced substantially and most of the interfering radionuclides are eliminated.

Mass spectrometry is a sensitive method for the determination of ^{226}Ra and ^{228}Ra and their isotope ratio. Three types of mass spectrometry have been used for the determination of ^{226}Ra and ^{228}Ra: thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS*)* and accelerator mass spectrometry (AMS).

TIMS is one of the most sensitive and most accurate mass spectrometric techniques. The major disadvantage is the complicated radiochemical separation procedure necessary to concentrate the Ra in the small source volume, to separate the matrix components, to remove possible interferences and to prepare the source on the filament. The detection limit for ^{226}Ra is about 40 µBq [2.63], better than the sensitivity of alpha spectrometry. The detection limit of 12 mBq for ^{228}Ra is comparable to that of beta counting.

ICP-MS is the most frequently used mass spectrometric technique for the determination of ^{226}Ra concentration and the ^{228}Ra/^{226}Ra isotope ratio. The detection limit of ICP-MS varies from 10^{-15} g to 10^{-8} g, and the precision varies between 0.1 and 0.5 %. Better precision of isotope ratio measurements can be achieved by using multi-ion collector devices in sector field ICP-MS [2.78].

AMS is one of the most sensitive measurement methods for those elements that form negative ions, but it is a very expensive technique, hence there are fewer than a hundred AMS facilities worldwide. Many of the interferences are suppressed or eliminated during the combined ionization, acceleration and mass analysis steps. Isotopic ratios below 10^{-10} can be measured by AMS. A detection limit of 10^7 atoms or 0.1 mBq for ^{226}Ra and 40 mBq for ^{228}Ra has been reported by Tims et al. [2.79] using test solutions. This sensitivity is comparable to the alpha spectrometric method for ^{226}Ra and to LSC and beta counting methods for ^{228}Ra. The major advantage of AMS for Ra measurements is the ability to measure both isotopes within a short time. Table 2.5 provides a comparison of the techniques under described measurement conditions adapted from Refs [2.80, 2.81] and updated here.

TABLE 2.5. COMPARISON OF THE RADIOMETRIC AND MASS SPECTROMETRIC METHODS FOR THE DETERMINATION OF ^{226}Ra AND ^{228}Ra BASED ON METHOD SENSITIVITY AND ANALYSIS TIME

Sample type	Detection method	Detection limit (mBq)	Sample preparation time	Delay time	Counting time (h)
Ra-226					
Environmental samples	γ-spectrometry	0.1–1	None	3 weeks	5
Water	γ-spectrometry	0.2	1 h	3 weeks	40
Environmental samples	LSC	0.3–1.4	2 h	30 days	6
Water (simultaneous)	LSS	10	2 h	None	2

TABLE 2.5. COMPARISON OF THE RADIOMETRIC AND MASS SPECTROMETRIC METHODS FOR THE DETERMINATION OF ^{226}Ra AND ^{228}Ra BASED ON METHOD SENSITIVITY AND ANALYSIS TIME (cont.)

Sample type	Detection method	Detection limit (mBq)	Sample preparation time	Delay time	Counting time (h)
Environmental samples	α-spectrometry	0.2 -0.5	2–4 days	None	48
Environmental samples	TIMS	0.037	4–5 h	None	0.5
Water	ICP-MS	0.1–0.5	2–4 h	None	0.2
Water	ICP-MS flow injection separation	0.34	0.5 h	None	0.4
Water	AMS	0.1	3–5 h	None	0.5

Sample type	Detection method	Detection limit (mBq)	Sample preparation time	Delay time	Counting time (h)
Ra-228					
Environmental samples	α-spectrometry	0.2	2–4 days	6–12 months	48–72
Water	LSC	25	1–2 days	None	1
Water (simultaneous)	LSS	40	2 h	None	2
Water	GM counter	15	4–8 h	None	2
Water	γ-spectrometry	0.4	1 h	24 h	40
Environmental samples	TIMS	12	4–5 h	None	0.5
Water	AMS	40	3–5 h	None	0.5

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Chapter 3

RADIUM IN THE ENVIRONMENT

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3.1. INTRODUCTION

Natural radionuclides fall into two categories: cosmogenic and primordial radionuclides. Cosmogenic radionuclides, such as carbon-14 and beryllium-7, are present because they are continually being formed in the atmosphere due to cosmic rays. Cosmic radiation enters the Earth's atmosphere and interacts with gaseous and particulate constituents to produce a variety of cosmogenic radionuclides. These interactions often trigger a cascade of secondary reactions producing additional cosmogenic radionuclides.

Primordial radionuclides originate mainly from fusion reactions in the interior of supernovae. They have been present since the formation of the planet 4.6×10^9 years ago. Because their half-lives are so long (comparable to the age of the Earth), most of them have not yet completely decayed and can be detected. Primordial radionuclides include ^{232}Th, ^{40}K, ^{87}Rb, ^{244}Pu, ^{238}U and ^{235}U. Primordial radionuclides also include ^{242}Np, the parent of the neptunium decay series, whose half-life is much shorter than the Earth's age and that has decayed away completely. Since primordial radionuclides have such long half-lives and relatively low abundance, they are of little significance in terms of environmental concentration and dose, with the exception of ^{238}U, ^{40}K and ^{87}Rb. Here the concern is for U as a heavy metal rather than a radionuclide.

The vast majority of natural radiation detected on Earth is from the radionuclides of the three natural decay series. They have shorter half-lives than the parent primordial radionuclides, and are therefore responsible for a significant portion of the radiation doses from natural radiation received by humans. One such naturally occurring radionuclide is ^{226}Ra, which is a radiogenic daughter of U decay and is found in various types of rock and geologic formations including U ores.

NORM consists of any material containing only naturally occurring radioactive elements, such as U, Th and K, and any of their decay products, such as Ra and Rn. Material in which the activity concentrations of the naturally occurring radionuclides have been changed by a process is included in NORM. Generally, NORM contains natural radionuclides in low or moderate concentrations, e.g. some granites and phosphate sedimentary rocks, and may be found on the Earth's surface or in its crust. The radionuclides can be brought to the surface and moved around the biosphere either through natural processes such as exhalation of radon gas from soils to the atmosphere, or through artificial processes such as extraction of groundwater and metal mining. Some NORM may contain high concentrations of radionuclides, such as U ores and monazite sands. Natural events, including volcanic eruptions, seismic events and forest fires, also impact the distribution of natural radiation.

Human activities that exploit natural resources (such as groundwater treatment, mining and processing of ores, the combustion of fossil fuels and the production of natural gas and oil) can enhance radionuclide concentrations in one of two ways. First, the concentrations of NORM can be enhanced above natural levels in a product, by-product or residue as a consequence of the raw material processing. Secondly, the bioavailability of radionuclides in by-products and residues can be enhanced as a consequence of physicochemical changes or simply due to the method by which the residues are managed.

There are many processes by which human activities result in increased activity concentrations, including those listed in Table 3.1.

TABLE 3.1. PROCESSES BY WHICH HUMAN ACTIVITIES RESULT IN INCREASED ACTIVITY CONCENTRATIONS

Process	Mechanism/Result
Groundwater extraction for use as drinking water	Changes to the chemical boundary conditions (pH, redox potential and gas partial pressures) and chemical equilibrium, leading to the precipitation of scales (which co-precipitate, for instance, Ra)
Formation water in oil and natural gas extraction	Mixing corrosion resulting from the mixing of waters with different CO_2 partial pressures, leading to the dissolution of scales
Combustion processes	Volatilization of certain nuclides, such as lead and polonium, and concentration of non-volatile nuclides, such as Ra, in the ash
Physical disaggregation (such as crushing of ore or waste rock)	Enhancement of dissolution and dispersal by increasing surface areas
Sedimentation in sludge ponds	Accumulation of naturally occurring radionuclides, which are often associated with heavy minerals, such as rutile and zircon
(Preferential) adsorption on clays or organic sedimentary fractions	Enhancement of concentrations in these fractions Size fractionation (sieving, flotation, etc.) leading to further concentration enhancement in fines and slimes

Radioactive residues are found in a range of industrial activities, namely:

- Mining and milling of metallic and non-metallic ores;
- Production of phosphate fertilizers;
- Production of non-nuclear fuels, including coal, oil and gas;
- Extraction and purification of water, for example as drinking water and for the generation of geothermal energy;
- Production of industrial minerals and building materials.

Anthropogenic activities can also result in the creation of artificial radionuclides from stable isotopes. Sources of anthropogenic radiation include releases from nuclear weapons testing, releases from nuclear industries, local releases due to nuclear weapons and releases from nuclear medicine and research laboratories.

Because Ra has four naturally occurring isotopes with half-lives ranging from 3.7 d to 1600 a, it is a powerful tracer of environmental processes. The distributions of these isotopes may be modelled to reveal important information about the environment. Thus, Ra is not only a potential environmental problem, but also a potential environmental problem solver.

3.2. RADIUM IN PARENT ROCKS AND SOILS

3.2.1. Parent rocks

The Earth's crust consists of a variety of rocks belonging to igneous, sedimentary and metamorphic groups which are 95% magmatites, 4% slate or shale, 0.68% sandstone and 0.32% carbonate rocks [3.1]. Concentrations of naturally occurring radionuclides in igneous rocks are usually higher compared to sedimentary ones, excepting shale, deep-sea sediments and phosphate rocks, while metamorphic rocks have concentrations similar to those of the rocks from which they were derived. High silica igneous rocks contain relatively higher U concentrations compared to such basic low silica igneous rocks as basalt.

Isotopes of Ra are progeny of the U, Ac and Th natural radioactive decay series of radioactive elements and are therefore widely distributed in the Earth's crust. The estimated average ^{238}U concentration in the continental crust is 32.9 Bq/kg [3.2] and, assuming radioactive equilibrium with ^{238}U, the crustal ^{226}Ra activity is expected to be of an equivalent order. Although it can be anticipated that in most igneous rocks Ra isotopes are present in equilibrium concentrations with their precursors, the impact of some environmental factors, such as weathering, can change ratios between ^{226}Ra or ^{228}Ra and their precursors, i.e. ^{230}Th and ^{232}Th, because of the differences in their environmental mobility. These phenomena and distribution of Ra in different environments are discussed in detail elsewhere [3.3–3.7].

Variations of Ra activity concentrations in the various rocks can differ from those of U and Th and require further assessments. A summary of ^{226}Ra concentrations in various rocks is presented in Table 3.2 [3.3, 3.8].

TABLE 3.2. Ra-226 CONCENTRATIONS IN VARIOUS ROCKS

Rock group	Type of rock	^{226}Ra concentration (bq/kg)
Magmatite	Volcanic rocks	48–137
	Base lava	33
	Granite	0.037–185
	Basalt	11–48
Magmatic rocks	Acid	111
	Intermediate	96
	Base	11–48
Sedimentary rocks	Shale (Alume slate)	14.8–2220
	Bitumen slate	629–1040
	Sedimentary rocks	9.2–15
	Lime	5–18
	Sandstone	7–55
	Phosphate rocks	148–1480
	Carbonate	26–30
	Clay rocks	55

The highest ^{226}Ra concentrations were observed in shale, bitumen slate and volcanic and phosphate rocks followed by granites, clay rocks and sandstone and, finally, sedimentary rocks, lime and carbonate. The high ^{226}Ra levels in shale and bitumen slate are likely due to associations of clay rich material of organic origin, while phosphate rocks of sedimentary origin are well known as minerals rich in U.

Granites and basalts tend to have nearly similar mean ^{226}Ra concentrations. At the same time, granites have a much wider range of ^{226}Ra occurrences, with especially high concentrations in rocks with a substantial occurrence of U and Th. Data from Conway, in New Hampshire [3.9], and the Colorado Front Range [3.10], both in the United States of America, illustrate such a phenomenon.

3.2.2. Soil

Soil properties, including concentrations of naturally occurring radionuclides in the soil, depend to a large extent on the parent rock properties. Rocks are continuously affected by many environmental factors which result in soil formation such as changes in temperature, water, flora and fauna, etc. In particular, because of its weathering from the host rocks and its further dispersion in the environment, Ra can be transported and deposited as loess, silt placers and tertiary soil [3.3]. In the soil, Ra behaves very much like other elements from Group 2 (alkaline earth metals) of the Mendeleyev periodic table, namely, Ca, Sr and especially Ba. Ion exchange processes play an important role in the migration of Ra in soil, and in this respect it has a close similarity to Ba owing to its large ionic radius. The ion exchange capacity characteristics of different types of soil vary considerably and this has a significant influence on the distribution of Ra in soil. Radium dissolved in groundwater (or surface water) is transferred with the water flow until it becomes adsorbed in the soil [3.3]. Some of the Ra data available for different types of soil are given in Table 3.3 [3.3, 3.11–3.18], while data for different countries are presented in Table 3.4.

TABLE 3.3. Ra-226 CONCENTRATIONS IN SOILS

Landscape	Type of soil	Texture	Location	^{226}Ra (Bq/kg)	Reference
Tundra	—	—	Russian Federation[a]	140 ± 20	[3.11]
Taiga	Soddy-podzolic	Loam	Russian Federation[a]	280 ± 70	[3.11]
	Soddy-podzolic	Loam	Russian Federation	14–44	[3.11]
Mixed forest	Podzol	Loam	Russian Federation	30 ± 3.7	[3.12]
	Soddy-podzolic[a]	Light loam	Russian Federation	22.6 ± 1.0	[3.13]
Mixed forest	Grey forest soil	Loam	Russian Federation	28.1 ± 0.7	[3.13]
	Bog-podzol	Organic	Russian Federation	24 ± 4	[3.12]

TABLE 3.3. Ra-226 CONCENTRATIONS IN SOILS (cont.)

Landscape	Type of soil	Texture	Location	^{226}Ra (Bq/kg)	Reference
Mixed forest	Chernozem	Clay	Russian Federation	37 ± 4	[3.12]
Deciduous forest	Grey forest	Loam	Russian Federation	17–33	[3.12, 3.14]
Meadows, steppe	Chernozem, brown earth[b]	Clay, heavy loam	Russian Federation	30.7 ± 2.5	[3.13]
	Chernozem	Clay	Russian Federation	33 ± 3.1	[3.15]
Wet subtropics	Red clay	Clay	Florida, USA	7.4	[3.16]
Dry subtropics	Red earth	Heavy loam	Former USSR	40.7–54	[3.15, 3.17]
—	Lime	Loam	—	3.7	[3.3]
Desert	Light brown desert soil		Former USSR	70.3–126	[3.3]
Atlantic maritime	Podzol soils	Sandy loam	Canada	30	[3.18]
Mixed wood plains	Grey brown Luvisol and related Gleysol phase soils	Loam	Canada	20	[3.18]
Boreal shield	Podzol soils	Sandy loam	Canada	20	[3.18]
Mixed wood plains	Calcareous Brunisol soils	Sandy loam	Canada	30	[3.18]
Boreal shield	Heavy clay grey Luvisol soils	Clay loam	Canada	30	[3.18]
Boreal shield	Acidic Brunisol (some marginal podzol) soils	Sand	Canada	20	[3.18]

[a] Area with evaluated natural background, Komi Republic.
[b] Samples taken from arable soil.
— = no data available.

The data of Table 3.3 show that ^{226}Ra concentrations in soil in normal areas (i.e. not areas of high natural background) vary from 3.7 to 126 Bq/kg. The highest mean values in a range from 70 to 126 were found to be in light brown desert soil. The lowest (mean) value was found in lime (3.7 Bq/kg), while intermediate values vary within a very narrow range (20–40 Bq/kg) with the soil texture.

Available data on Ra measurements in soil in various countries of the world have been reported in an UNSCEAR publication [3.6]. Table 3.4, adapted from Ref. [3.6], shows that ^{226}Ra concentrations in soil vary across a wider range compared to the data of Table 3.3, most likely because of the wider range of soil types investigated, the inhomogeneity of the soils studied, the wider range of U and Th concentrations in the parent rocks and other properties favouring Ra retention in the topsoil. Even within some countries, the ranges of ^{226}Ra concentrations in soils covered the whole range of the ^{226}Ra concentrations presented in Table 3.4. For example, this is the case for Switzerland (10–900 Bq/kg) and for China (2–440 Bq/kg).

TABLE 3.4. Ra-226 CONCENTRATIONS IN SOIL

Region	Country	Mean (Bq/kg)	Range
Africa	Algeria	50	5–180
	Egypt	17	5–64
North America	Costa Rica	46	11–130
	United States of America	40	8–160
East Asia	Bangladesh	34	21–43
	China	32	2–440
	India	29	7–81
	Japan	33	6–98
	Kazakhstan	35	12–120
	Malaysia	67	38–94
	Thailand	48	11–78

TABLE 3.4. Ra-226 CONCENTRATIONS IN SOIL (cont.)

Region	Country	Mean (Bq/kg)	Range
West Asia	Armenia	51	32–77
	Islamic Republic of Iran	28	8–55
	Syrian Arab Republic	23	10–40
North Europe	Denmark	17	9–29
	Estonia	35	6–310
	Norway	50	—
	Sweden	42	12–170
West Europe	Belgium	26	5–50
	Germany	—	5–200
	Ireland	60	10–200
	Luxembourg	35	6–52
	Netherlands	23	6–63
	Switzerland	40	10–900
	United Kingdom	37	—
East Europe	Bulgaria	45	12–210
	Czech Republic	—	3.7–141
	Hungary	33	14–76
	Poland	26	5–120
	Romania	32	8–60
	Russian Federation	27	1–76
	Serbia	22.5	10–41
	Slovakia	32	12–120
South Europe	Croatia	54	21–77
	Cyprus	17	0–120
	Greece	25	1–240
	Portugal	44	8–65

TABLE 3.4. Ra-226 CONCENTRATIONS IN SOIL (cont.)

Region	Country	Mean (Bq/kg)	Range
	Slovenia	41	2–210
	Spain	32	6–250
Median		35	17–60
Population weighted average		32	

— = no data available.

The average worldwide population weighted value for ^{226}Ra concentration in soil of 32 Bq/kg was reported based on these data from the UNSCEAR [3.6]. However, there are some areas in the world where the normal range of variation of naturally occurring radionuclides in soils or waters is greatly exceeded. These areas include the well known sites of Kerala and Tamil Nadu in South India, with sands containing monazite with a high Th content, and Ramsar in the Islamic Republic of Iran (Iran) where high levels of ^{226}Ra in water have been identified. Some of the data available for high background radiation areas are given in Table 3.5 [3.3, 3.6, 3.19, 3.20].

The activity concentrations of ^{226}Ra presented in Table 3.5 vary across a much wider range than those in Table 3.4 where similar information was given for normal areas. Maximum values were found to be for Ramsar, Iran, and the Komi Republic of the Russian Federation, where ^{226}Ra activity concentrations were three orders of magnitude higher than the average worldwide value of 32 Bq/kg reported by the UNSCEAR [3.6].

TABLE 3.5. EXAMPLE OF AREAS OF HIGH ^{226}Ra CONCENTRATIONS IN SOIL

Region /Country	Site	^{226}Ra (Bq/kg)	Origin of high Ra concentrations	Reference
Asia				
India	Kerala	7.8–2500	Thorium areas	[3.6]
Indonesia	West Java	2.4–422	Thermal water	[3.6]
Islamic Republic of Iran	Ramsar	80–50 000	Thermal water	[3.6]
	Mahallat	500–7300	Thermal water	[3.6]
Europe				
Czech Republic	Central Bohemia, Pluton middle area	76–275	Uranium and thorium areas of volcanic intrusion	[3.6]
France	Ambazac Mountain	950–8860	—	[3.3]
Russian Federation	Komi Republic	259–71000	—	[3.19]
Spain	South Galicia, Arribes del Duero	60–250	—	[3.6]
South America				
Brazil	Phosphate area, P.E.	29–207	Uranium area	[3.6]
	Araxa	700–42400	—	[3.3]
	Tapira	800–29000	—	[3.3]
Pacific				
New Zealand	Niue	6920–12 400	Weathered limestone enriched by volcanic ash	[3.3, 3.20]

3.3. RADIUM IN GROUNDWATER

Radium in groundwater can arise from natural sources, resulting from the interaction of groundwater with Ra bearing materials such as rocks, soil, ore bodies and other source materials. The process of concentration of ^{226}Ra and its parent nuclides in percolating groundwater is affected by the availability and solubility of the nuclides in the rocks through which the groundwater percolates, as well as by rock permeability, the presence of ionic materials, the acidity of the medium, etc. All of these parameters are highly variable and explain why groundwater ^{226}Ra and ^{238}U concentrations may differ by three to five orders of magnitude [3.21] (Table 3.6) [3.22–3.42].

Radium and other naturally occurring radionuclides can also be indirectly released through exploitation of the radioactive minerals (e.g. U, Th) that are part of the nuclear fuel cycle. This is also true for the mining and processing of other conventional minerals of commercial importance, such as the phosphatic minerals — apatite ($Ca_5(P0_4)_3F$, Cl, OH), copper, gold, lignite, coal and other such ores — owing to the presence of U and its long lived daughter products in the minerals.

In particular, during in situ mining, well patterns are intended to create a hydrodynamically well controlled flow regime for the lixiviant, thus minimizing dispersion losses and the contamination of surrounding aquifers. Nevertheless, in situ leaching processes may result in the development of contaminated water plumes that extend beyond the boundary of producing well fields. Examples of this have been reported in the Cu and U mining industries [3.43, 3.44]. The contaminants most often found in groundwater that exceeds the drinking water contaminant limits include U, Ra, Se, Mo, Mn, As, nitrate and sulphate.

Geothermal springs and geothermal energy production are another source of ^{226}Ra to groundwater [3.3]. Radium is slightly soluble and consequently can be brought to the surface and co-precipitated with Ba and Ca salts as scale on the inside surfaces of drilling and production equipment, similar to the case of oil and gas production. Sludge is formed by precipitation and sedimentation during the cooling process. Disposal of both scales and sludges into landfill facilities has the potential for long term radionuclide transport through groundwater if a site liner fails.

Similarly, a residue of drinking water and sewage water treatment is NORM containing sludge. The disposal of this sludge in lagoons, evaporation ponds and landfills may result in contamination of underlying groundwater bodies.

TABLE 3.6. RADIUM ISOTOPE CONCENTRATIONS IN GROUNDWATER

Region	Country/Location	Groundwater Source	Description of Source	^{226}Ra (mBq/L)	^{228}Ra (mBq/L)	Reference
Europe	Austria/Salzburg	Well water	—	<3.7–270	—	[3.22]
	Finland/Helsinki	Drilled wells	—	<3.7–9470	14.8–207	[3.23]
	—	Drilled wells	—	122–1900	<18.5–570	[3.24]
	Bulgaria	Bottled mineral water	—	392	n.d.	[3.25]
	France	Bottled mineral water	—	163	218	[3.25]
	Greece	Bottled mineral water	—	237	263	[3.25]
	United Kingdom/Bath	Thermal springs	—	374–525	—	[3.26]
Asia & the Far East	India/Kalpakkam	Well water	—	1.11–77.7	20.7–23.3	[3.26]
	India/Maharashtra State	Thermal springs	—	40.7–2600	—	[3.27]
	Japan	Thermal springs	—	529–655	—	[3.28]
		Thermal springs	—	1300–7840	—	[3.28]
	Lebanon	Bottled mineral water	—	255	240	[3.28]
	Saudi Arabia	Bottled mineral water	—	333	222	[3.28]
	Saudi Arabia	Raw water	—	699	174	[3.28]
	Taiwan, China	Thermal springs	—	1.85–588	—	[3.29]
	United Arab Emirates	Bottled mineral water	—	292	203	[3.25]

TABLE 3.6. RADIUM ISOTOPE CONCENTRATIONS IN GROUNDWATER (cont.)

Region	Country/Location	Groundwater Source	Description of Source	^{226}Ra (mBq/L)	^{228}Ra (mBq/L)	Reference
Americas	USA/Ottawa County, OK	Well water	Public water supply	3.7–570	—	[3.30]
	USA/Florida	Well water	Untreated water supply	7.4–122	—	[3.31]
	USA/Illinois	Well water	Untreated water supply	0.74–836	—	[3.32]
	USA/Utah	Well water	Artesian wells	<37–740	—	[3.33]
	USA/South Carolina	Well water	—	100–981	174–440	[3.34]
	USA/Iowa	Well water	Public supply	3.7–1780	—	[3.35]
	USA/Iowa	Well water	Ra-228/Ra-226 = 0.4–25	66.6–925	<22.2–233	
	USA/Boise, Idaho	Well water	Shallow and deep wells	3.8	—	[3.36]
	USA/Joliet, Illinois	Well water	Deep wells	242	—	[3.36]
	USA/Miami, Florida	Well water	Shallow wells	17.7	—	[3.36]
	USA/Memphis, Tennessee	Well water	Shallow and deep wells	7.8	—	[3.36]
	USA/Wichita, Kansas	Well water	Deep wells	8.4	—	[3.36]
	USA/Grants	Groundwater	Uranium mining district	1.9–1960	—	[3.37]
	USA/Texas (South Texas)	Groundwater	Uranium mining and milling	14.8–6290	—	[3.38]
	USA/Florida	Groundwater	Phosphate mining district	n.d.–2810	—	[3.39]

TABLE 3.6. RADIUM ISOTOPE CONCENTRATIONS IN GROUNDWATER (cont.)

Region	Country/Location	Groundwater Source	Description of Source	^{226}Ra (mBq/L)	^{228}Ra (mBq/L)	Reference
	USA/Sarasota, Florida	Groundwater	Phosphate mining district	55.5–903	—	[3.39]
	USA/Western USA	Geothermal water	Exploitation of geothermal water	<1.52–55,500		[3.40]
	Brazil	Groundwater	Mineral water from various parts of Brazil	n.d.–3480	n.d.–5610	[3.41]
Australia	Yeelirrie	Groundwater	Proximal to uranium deposits	18.5–33,400		[3.42]

n.d. = not detectable
— = no data available

3.4. RADIUM IN FRESHWATER

Radium in freshwater can arise from natural sources such as groundwater inflow, sediment resuspension, resolubilization of sediment bound radionuclides and from air through precipitation and particle deposition. While ^{226}Ra and ^{228}Ra activity concentrations have a wide range in groundwater, depending upon the source characteristics in the study region and the ionic strength of the groundwater, ^{226}Ra and ^{228}Ra activities in surface water are low and lie within a relatively narrow range of concentrations (Table 3.7 [3.3, 3.29, 3.31, 3.32, 3.36, 3.45–3.78]).

Activities in river water generally range between 0.5 and 20 mBq/L for ^{226}Ra, though enhanced concentrations (of up to 300 mBq/L) have been reported. For ^{228}Ra, data are scarce but the range is similar to that for ^{226}Ra [3.79].

For other surface areas, such as lakes, ^{226}Ra concentrations are also within a narrow range (0.5–15 mBq/L), similar to that observed for river water [3.79].

TABLE 3.7. RADIUM ISOTOPE CONCENTRATIONS IN RIVERS AND LAKES (mBq/L)

Country	^{226}Ra	^{228}Ra	Reference
Rivers and streams:			
Australia: Magela Creek	1.8	0.9	[3.45]
Austria: Danube River	18.5	—	[3.3, 3.46]
Brazil: Amazon River	0.78–1.22	0.87–1.07	[3.3, 3.47]
Canada	4.07–13.7	—	[3.3, 3.48]
China	7.4–18.5	—	[3.3, 3.29]
Former Czechoslovakia	3.7–292	—	[3.3, 3.49]
Egypt: Nile River	3.7–155	—	[3.3, 3.50]
Germany	2.59–31	—	[3.3, 3.51]
India: Ganges River	20–48	—	[3.3, 3.52]
India: Ganges River	3.33	1.63–2.6	[3.3, 3.53]
United Kingdom: River Thames	18.5	—	[3.3, 3.54]
USA: Mississippi River	0.37–40	—	[3.3, 3.36, 3.55]
USA: Hudson River	1.17	—	[3.3, 3.56]
USA: Suwannee River	7.4	—	[3.3, 3.31]

TABLE 3.7. RADIUM ISOTOPE CONCENTRATIONS IN RIVERS AND LAKES (mBq/L) (cont.)

Country	^{226}Ra	^{228}Ra	Reference
Lakes:			
Australia: Alligator Rivers Region	3–50	—	[3.57]
Canada (SK): reference areas	5.0–9.0	—	[3.58–3.60]
Canada (SK): mining areas	5.0–1,450	—	[3.58–3.70]
Germany : Bagger Lake	2.22–2.59	—	[3.3, 3.71]
Germany : Black Forest	16.7–145	—	[3.3, 3.72]
India	3.7–14.8	—	[3.3, 3.73]
Italy	0.52–0.74	—	[3.3, 3.74]
Scotland (UK): Loch water	0.37–4.44	—	[3.3, 3.75]
USA: Illinois	2.20–48.8	—	[3.3, 3.32]
USA: Lake Ontario	1.48–62.9	—	[3.3, 3.76]
Former USSR	7.4	—	[3.3, 3.77]
Former Yugoslavia	39	—	[3.3, 3.78]

— = no data available

Studies of ^{226}Ra distributions in surface water surrounding regions of U deposits are of considerable interest. The high ^{226}Ra concentrations, unaccompanied by similar ^{228}Ra activities (Table 3.7), are due to the presence of U bearing phosphorites in the drainage basin [3.80]. Radium-226 concentrations in Brazilian river water in the vicinity of the U mining area at Pocos de Caldas were measured as part of a baseline study in 1977–1978 [3.81]. The concentrations are within a range of 7.4–222 mBq/L. However, in most river water samples, ^{226}Ra levels were generally under 37 mBq/L, with the exception of small streams originating in a region of exploratory U mining, where the concentration was 1100 mBq/L. Limited seasonal studies did not appear to show much variation in Ra concentrations in this water.

Monitoring of Magela Creek (Alligator Rivers Region, Australia) from 2001 to 2011 gave median (SD) ^{226}Ra concentrations of 1.8 (0.9) mBq/L [3.81]. Concentrations consistently decrease over the course of the wet season. Measured ^{226}Ra/^{228}Ra activity ratios were within the range of 1.7–2.1. Concentrations in water of the water bodies of the region vary considerably, depending on concentrations in the sediments and the amount of suspended matter in the water column; Ra levels tend to rise during the dry season [3.57].

Environmental monitoring data for U mining/milling sites in northern Saskatchewan show baseline ^{226}Ra values that range from 5.0 to 20 mBq/L, with values that fall between 5.0 and 3 000 mBq/L in mining areas. Baseline ^{226}Ra values reported in surface waters in Florida were relatively higher compared to those measured in northern Saskatchewan, although comparable values have been found in mining areas (Table 3.8, [3.58–3.70, 3.82, 3.83]).

TABLE 3.8. RADIUM-226 ACTIVITY CONCENTRATIONS IN SURRFACE WATERS FROM REFERENCE AND EXPOSURE SITES IN NORTH AMERICA

Type of site	Country/region	Ecosystem sub-category	Ra-226 activity concentration (Bq/L)			
			Mean	N	SD	References
Reference	USA/Florida	Lake	4.93×10^{-1}	9	1.20E-01	[3.82]
	Canada/ Saskatchewan	Lake	6.58×10^{-3}	26	1.84E-03	[3.58–3.60]
	Canada/ Saskatchewan	Stream	2.00×10^{-2}	19	3.56E-18	[3.83]
Exposure	USA/Florida	Lake	1.2	20	5.69×10^{-1}	[3.82]
	Canada/ Saskatchewan	Lake	1.52×10^{-1}	364	3.77×10^{-1}	[3.58–3.70]
	Canada/ Saskatchewan	Stream	2.53	37	1.08	[3.69, 3.70]

One source of Ra in these regions is the flow of groundwater to surface water bodies. As mentioned above, the groundwater interacts with Ra bearing rocks and ore bodies and transports Ra and other naturally occurring radionuclides to the surface water. Radium isotopes have been used extensively to quantify such discharges [3.83].

Human activities can also contribute to the dispersal of NORM into surface water. The main pathway for mining and milling operations to disperse NORM into the environment is through water. Mine water generated at mines and released to surface water contains radionuclides such as Ra due to its interaction with radionuclide bearing rock. The chemical and radiological composition of mine water varies by site and is dependent on the geochemistry of the ore body and the surrounding area.

A recently reported area of concern is the use of water mixed with sand and chemicals at high pressures to fracture rock formations and release natural gas, a process known as hydrofracking. A large fraction of the water injected into each well resurfaces in the first few weeks of the process. This water may carry high activities of ^{226}Ra and ^{228}Ra, up to 620 Bq/L of ^{226}Ra and 95 Bq/L of ^{228}Ra [3.85]. The wastewater may be sent to plants unable to process it; they would therefore simply discharge their partially treated waste into rivers.

In addition, many (sedimentary) rocks contain sulphidic minerals such as pyrite. Upon exposure to ambient air, these sulphides are oxidized to sulphuric acid. These acidic conditions can accelerate the weathering of the mining debris and the dissolution and leaching of mineral constituents, including radionuclides, owing to their higher solubility at low pH values [3.86, 3.87]. This phenomenon, known as acid mine drainage (AMD) or acid rock drainage (ARD), is a major worldwide problem and has been a subject of significant scientific and technical attention for some time. Elevated radionuclide concentrations have been reported frequently in ARD. For instance, ^{238}U and ^{226}Ra concentrations of 175 and 0.29 Bq/L, respectively, have been measured in the ARD of the U mining and milling facility of Poços de Caldas, Brazil [3.88].

Mineral and metal processing activities can also result in a release of NORM to the environment. For example, in tin slag processing, large volumes of water are used to separate valuable minerals from sands and sediments through physical separation. Although the method used is effective in physically separating the minerals bearing radionuclides from unwanted sands and sediments, the recycling of water and the use of recycling ponds have directly contributed to the accumulation and enhancement of NORM, including ^{40}K, ^{238}U, ^{226}Ra and ^{232}Th in the environment surrounding the processing plant [3.89–3.92].

Finally, human activity can also promote the cycling of Ra from groundwater through surface water and into sediments. Large amounts of ^{226}Ra are released into the environment with wastewater from coal mines. In the mine, or after being transferred to the surface, wastewater containing Ra^{2+} and Ba^{2+} mixes with natural water containing SO_4^{2-} ions, and Ra co-precipitates as $RaSO_4$ with $BaSO_4$. The activity of such precipitates was found to be as high as 1000 Bq/g. Large amounts of such sediments were observed inside some of the mines and on the bottom and banks of the deposition ponds and their outlet canals [3.93].

3.5. RADIUM IN SEAWATER

3.5.1. Oceans

In the open ocean, the major processes affecting the distribution of the long lived Ra isotopes are supply from continents and the seabed and removal by radioactive decay and particle scavenging. Because its mean life is on the order of the mixing time of the ocean, ^{226}Ra is distributed throughout the water column. In spite of the long half-life of ^{226}Ra, significant variations occur within the ocean due to the processes of decay and particle scavenging superimposed on the mixing pattern of the world ocean (Table 3.9 [3.94]).

Since the mean life of ^{228}Ra is much shorter than the vertical ocean mixing time, its distribution is restricted to regions near its source of input, namely surface and near bottom waters in contact with sediments. Because horizontal mixing is much faster than vertical mixing, ^{228}Ra derived from the continents is spread throughout the surface ocean.

TABLE 3.9. VARIATIONS OF ^{226}Ra IN THE WORLD'S OCEANS

Water body	^{226}Ra dpm/100 kg	^{226}Ra (mBq/L)
Atlantic Ocean surface water	7.9 ± 0.8	0.135 ± 0.014
Indian Ocean surface water	8.6 ± 1.7	0.147 ± 0.029
Pacific Ocean surface water	7.1 ± 1.4	0.122 ± 0.024
Antarctic Ocean surface water	15.1 ± 2.9	0.258 ± 0.050
N Atlantic Ocean deep water	14.8 ± 2.6	0.253 ± 0.045
S Atlantic Ocean deep water	19.3 ± 3.3	0.330 ± 0.056
Antarctic Ocean deep water	21.3 ± 0.9	0.365 ± 0.015
S Indian Ocean deep water	26.8 ± 3.1	0.459 ± 0.053
N Indian Ocean deep water	27.8 ± 5.7	0.476 ± 0.098
S Pacific Ocean deep water	25.2 ± 3.7	0.431 ± 0.063
N Pacific Ocean deep water	34.6 ± 4.6	0.592 ± 0.079

3.5.2. Estuaries, lagoons and coastal waters

Because rivers, sediments and submarine groundwater discharge (SGD) add significant Ra to estuaries and coastal waters, it is here that we typically find the highest marine concentrations. In general, ^{226}Ra in estuaries is enriched by over an order of magnitude relative to the surface ocean; the other isotopes are generally enriched even more. Table 3.10 [3.80, 3.95–3.105] illustrates differences that occur in some estuaries and coastal waters.

TABLE 3.10. ACTIVITIES OF Ra ISOTOPES IN ESTUARIES OF THE WORLD

Water body	^{226}Ra (dpm per 100kg)	^{228}Ra (dpm per 100kg)	^{224}Ra (dpm per 100kg)	^{223}Ra (dpm per 100kg)	Reference
USA/North Inlet, SC	10–60	15–150	13–380	2–50	[3.95]
USA/Port Royal Sound, SC	30–80	60–210	30–130	9–21	[3.96]
USA/Okatee Estuary, SC	25–140	40–375	30–360	4–45	[3.97]
USA/St. Johns Estuary, FL	15–70	20–40	8–30	1–5	[3.80]
USA/Satilla Estuary, GA	4–40	5–80	6–70	4–16	[3.80]
USA/Savannah Estuary, GA	7–30	9–70	5–50	1–7	[3.80]
USA/Charleston Harbor, SC	10–40	8–70	4–55	1–13	[3.80]
USA/Winyah Bay, SC	6–30	6–40	4–50	1–5	[3.80]
USA/Tampa Bay, FL	90–280	45–175	20–180	15–145	[3.98]
USA/Loxahatchee Estuary, FL	15–75	7–24	9–35	2–13	[3.99]
USA/Waquoit Bay, MA					
USA/Great South Bay, NY	7–19	12–32	16–39	1–3	[3.100]
USA/Jamaica Bay, NY	60–100	160 –230	380–650	7–30	[3.101]
USA/Elkhorn Slough, CA	130 –255	60–560	180 –1100	12–175	[3.102]

TABLE 3.10. ACTIVITIES OF Ra ISOTOPES IN ESTUARIES OF THE WORLD (cont.)

Water body	^{226}Ra (dpm per 100kg)	^{228}Ra (dpm per 100kg)	^{224}Ra (dpm per 100kg)	^{223}Ra (dpm per 100kg)	Reference
Mexico/Celestium Lagoon, Yucatan	50 –1000	6–50	8–130	4–70	[3.103]
Italy/Venice Lagoon,	20–30	50–100	44–120	2–10	[3.104]
Australia/Zecks Lagoon	19–28	84–240	100–310	6–17	[3.105]

This table illustrates the explosion of new data on the distributions of Ra isotopes that has occurred in the past two decades. The addition of the short lived isotopes to these data sets allows estimates of estuarine flushing times. These estimates are fundamental to establishing fluxes of not only Ra, but also of nutrients, carbon and metals.

In addition to natural inputs and cycling of Ra in the marine environment, radionuclide discharges from the phosphate industry may be significant in some areas [3.106]. The main source of such discharges is fertilizer industry production of phosphoric acid from phosphate ore by using sulphuric acid. Several natural radionuclides of the U series, which are contained in the ore, are concentrated into the residue phosphogypsum, which can be discharged into surface waters, stockpiled on land or sold as a by-product. Phosphogypsum contains nearly all of the ^{226}Ra, ^{210}Pb and ^{210}Po present in the ore and smaller quantities of U and Th isotopes. Radium activity concentrations in the gypsum stacks range from background to 1700 Bq/kg [3.86]. The discharges of phosphogypsum into the sea cause the input of radiation from the fertilizer industry. The impact of this source on coastal areas has been shown to be significant as far as radiological doses are concerned. In Western Europe, all production facilities were closed down by the turn of the century, so this is no longer a source of radionuclides in most European marine environments. Most phosphate fertilizer is now produced in and imported from Africa and the Middle East, and this process is therefore still an important source of radionuclides to those marine environments.

3.6. RADIUM IN AIR

Radium is present in air in resuspended soil particles. A dust concentration in 50 μg/m^3 is often assumed for inhalation pathway evaluation. Based on this figure and the worldwide concentration of 32 Bq/kg for ^{226}Ra in soil, the concentrations in air can be estimated to be 1.5 μBq/m^3. This fairly low value is close to those observed in most areas. In particular, the UNSCEAR [3.107] reports representative values of 0.6 μBq/m^3, 1.2–3.3 and 0.8–32 μBq/m^3 for the United States of America, Germany and Poland, respectively. However, these values are presented only for temperate environments, and ^{226}Ra concentrations in air can vary according to climate and to location within a given climate. For example, ^{226}Ra concentration can be substantially higher in areas with a dry climate, and concentrations of U in sea air may be an order of magnitude lower at coastal locations than in continental or industrialized areas [3.108].

It is important to note that the dust loading of air contains substances other than soil, including considerable proportions of organic matter and, especially in wintertime, fly ash from coal burning [3.109]. The organic content is deficient in U compared to soil, but fly ash contains much higher concentrations of U.

The burning of coal and release of ash from furnaces represents another source for Ra in the atmosphere. In the combustion of coal at high temperature (up to 1700 ºC) which is required for electric energy generation, most of the coal’s mineral matrix is fused into a vitrified ash. The lighter ash, or fly ash, goes through the boiler together with hot flue gases and is released to the atmosphere. The fly ash can then be deposited to the ground, to vegetation and surface water and can even make its way into the groundwater.

Taking into account that the organic fractions of coal are eliminated within the combustion process, the concentration of Ra in ash is around one order of magnitude higher than in coal. Therefore, concentrations of naturally occurring radionuclides, including ^{226}Ra, in ash and slag from coal fired power stations are rather high, and mean values for ^{226}Ra concentration in escaping fly ash range from 44.3 to 2400 Bq/kg [3.86]. Major factors affecting the release of ^{226}Ra to the atmosphere are Ra concentrations in coal, ash content in coal, the temperature of combustion and the efficiency of emission control equipment such as flue gas filters and scrubbers.

Although this source is mainly responsible for local contamination of the environment, in some regions Ra from coal dominates in depositions.

3.7. RADIUM IN TERRESTRIAL PLANTS

Radium isotopes can be transferred to plants through two major pathways: root uptake from soil and foliar uptake from the interception of radionuclides on the external surfaces of plants. The relative contributions of these pathways can differ significantly depending on many factors including specific features of the organism, concentration of Ra in the atmosphere and in the soil, etc.

Radium is the heaviest member of the alkaline earth metals, a group of metals whose lighter members (Ca and Mg) play a very important role in plant growth and nutrition [3.110]. As Ra is highly electropositive, it reacts readily with many agents; most of these reaction products are insoluble. Radium also co-precipitates with Ba and Sr to form insoluble sulphates. Uptake of the bivalent ^{226}Ra is mostly controlled by factors affecting the soil exchange capacity. Radium has a high affinity for the regular exchange sites of the soil [3.111]. According to Simon and Ibrahim [3.110], organic matter adsorbs approximately ten times as much Ra as clay does. Increased exchangeable Ca, increasing pH and high soil sulphate content are reported to decrease Ra concentrations in plants [3.111, 3.112].

The association of Ra with organic matter was noted in many early geochemical/geophysical exploration programs. Such was also the case in a recent study of wetland soils (14–50% organic matter) in Ireland that showed ^{226}Ra/^{238}U activity ratios of up to 9.0; assuming initial isotopic equilibrium in soil (i.e. ^{226}Ra/^{238}U = 1.0), the elevated ratios suggest a loss of ^{238}U relative to ^{226}Ra [3.79]. As the largest ratios are seen in the depth zones that are only saturated at certain times of the year, this suggests that oxidizing conditions and leaching of uranyl complexes by percolating soil water may lead to such disequilibria; it reflects the relative immobility of Ra with respect to U under oxidizing conditions [3.79].

Radium concentrations in grassy and woody plants are given in Table 3.11 [3.3, 3.113–3.133], together with those in fungi, lichens and mosses. Overall, the ^{226}Ra activity concentrations in plants sampled in areas of normal radiation background are quite low. The highest concentrations are observed to be in mosses (57 Bq/kg), lichens (26 Bq/kg) and fungi (25 Bq/kg), followed by trees, bushes, grasses and finally by cereals and vegetables.

The high interception of radionuclides by lichens and mosses is one of the key factors explaining high accumulation of radionuclides in these species. Most lichens and mosses receive water and mineral nutrients mainly by foliar uptake. These plants lack a well developed root system and tend to accumulate contaminants from the atmosphere [3.134] by entrapping airborne particulates by both passive (which normally dominate) and active processes through extracellular ion exchange processes. A linear correlation between concentrations of radionuclides and heavy metals in lichens and mosses and bulk precipitation has been demonstrated in many studies. The lowest values are specific to temperate environments (e.g. Saskatchewan, Canada) with low releases of these radionuclides to the atmosphere, while for dry industrial areas with higher resuspension and release of naturally occurring radionuclides to the air, the concentrations are three- to fivefold higher.

Many fungi species are characterized by a marked ability to accumulate some radionuclides, particularly ^{137}Cs. However, transfer factors for many other radionuclides and heavy metals are also typically higher for fungi than for woody and grassy plants [3.135]. Overall, data on Ra concentrations in fungi are generally rather scarce. Baeza et al. [3.131] reported data for Ra concentrations in 71 fungi species sampled in Spain, with a mean value of 25 ± 22 Bq/kg (DW) and a range of 13–87 Bq/kg, although ^{226}Ra was above the detection limit only in 38.4% of the samples. Concentrations of ^{226}Ra in Saprophytic species (32 ± 27 Bq/kg (DW)) were higher than those in Mycorrhizal species (23 ± 21 Bq/kg (DW)); however, this difference was not identified as statistically significant.

Tree leaves can also be very effective accumulators of radionuclides because of their high interception ability. The concentrations of ^{226}Ra in tree and shrub leaves reported in Table 3.11 vary from 0.15 Bq/kg to 13.2 Bq/kg (DW). The highest values were observed to be for tropical forests, while in boreal forests concentrations of Ra in tree leaves were about one order of magnitude lower.

TABLE 3.11. Ra-226 ACTIVITY CONCENTRATIONS IN PLANTS IN NORMAL AREAS

Group of plants	Country	Comment	Ra (Bq/kg, DW)		Reference
			Mean±SD (GM/GSD)	Range	
Lichens					
Lichens	Canada	Saskatchewan	6.4	—	[3.113]
Lichens	Greece	4 sites, 23 species	26 ± 17	4 sites, 23	[3.114]
Lichens	Serbia	—	—	10.1–80.5	[3.115]
Lichens	Greece	—	9.0	—	[3.116]
Mosses					
Mosses	Canada	Saskatchewan	8.4 (FW)[a]	—	[3.113]
Mosses	Greece	—	57 ± 30	—	[3.114]
Mosses	Greece	—	9.0	—	[3.116]
Mosses	Yugoslavia	—	—	3.62–15.3 (FW)[a]	[3.3]

TABLE 3.11. Ra-226 ACTIVITY CONCENTRATIONS IN PLANTS IN NORMAL AREAS (cont.)

Group of plants	Country	Comment	Ra (Bq/kg, DW)		Reference
			Mean±SD (GM/GSD)	Range	
Mosses	Serbia	41 locations in Serbia	6.9^{b}	0.9 ± 0.1–25.8 ± 0.6	[3.117]
Mosses	Serbia	6 locations near Belgrade	22.4^{b}	6.1 ± 0.3–75 ± 10	[3.118]
Cereals (grain)					
Rice	Brazil	—	0.010/2.0^{c}	0.012–0.099	[3.119]
Rice	India	Bombay area	—	0.012–0.35	[3.120, 3.121]
Rice	India	Kalpakkam area	—	DL–0.105	[3.122]
Rice	USA	—	0.035	—	[3.123]
Rice	—	Worldwide estimate	0.2	—	[3.124]
Rice	India	Kartnataka	0.09	DL–0.1	[3.125]
Spring wheat	India	Punjab area	0.7/0.1^{c}	0.45–0.91	[3.126]
Spring wheat	India	Mahabaleshwar	<0.23	<0.23	[3.126]
Winter wheat	Belgium	—	—	0.06 ± 0.01–0.21 ±0.02	[3.127]
Vegetables					
Leguminous vegetables	Brazil	—	—	5.85–9.45	—
Leafy vegetables	Brazil	—	—	0.56–0.90	—
Root vegetables	Brazil	—	—	1.85–3.08	—
Leafy vegetables	India	Bombay area	—	0.34–3.05	[3.120]
Root vegetables	India	Bombay area	—	DL–2.40	[3.3]
Root vegetables	India	Kalpakkam area	—	0.14–0.25	[3.3]
	Germany	—	—	0.21–0.62	[3.125]
	UK	—	—	0.07–1.16	[3.125]

TABLE 3.11. Ra-226 ACTIVITY CONCENTRATIONS IN PLANTS IN NORMAL AREAS (cont.)

Group of plants	Country	Comment	Ra (Bq/kg, DW)		Reference
			Mean±SD (GM/GSD)	Range	
—	—	Worldwide estimate	—	0.27–0.41	[3.124]
Grass					
Mixture	Egypt	—	1.5 ± 0.1	—	[3.128]
Vicia cracca	Russian Federation	Komi Republic	7.7 ± 3.9	—	[3.129]
Dioscorea	India	Tropical forest, Kaiga	6.6 ± 1.9	—	[3.130]
Muli	India	Tropical forest, Kaiga	6.7 ± 1.8	—	[3.130]
Fruits (papaya)	India	Bombay area	0.23	—	[3.3]
Fungi	Spain		25 ± 22	13–87	[3.131]
Tree leaves					
River she-oak	India	Kalpakkam area	—	0.056–9.2	[3.3]
Kindal	India	Tropical forest, Kaiga	3.0	2.5–5.0	[3.130]
Slow match tree	India	Tropical forest, Kaiga	3.8	2.0–5.1	[3.130]
Birch	Czech Republic	—	0.25	0.05–0.43	[3.132]
Alder	Czech Republic	—	0.19	0.07–0.33	[3.132]
Elder	Czech Republic	—	0.15	0.04–0.27	[3.132]
Broom	—	—	0.7	—	[3.133]
Black pine	Greece	—	2.2	0.0–14.4	[3.114]
Black poplar	Greece	—	1.9	0.0–33.5	[3.114]

TABLE 3.11. Ra-226 ACTIVITY CONCENTRATIONS IN PLANTS IN NORMAL AREAS (cont.)

Group of plants	Country	Comment	Ra (Bq/kg, DW)		Reference
			Mean±SD (GM/GSD)	Range	
Almond	Greece	—	5.4	0.0–15.5	[3.114]
Firethorn	Greece	—	4.6	0.0–36.4	[3.114]
Tamarind	India	Tropical forest, Kaiga	5.7 ± 1.8	—	[3.130]
Mango	India	Tropical forest, Kaiga	3.6 ± 1.0	—	[3.130]
Burmese teak	India	Tropical forest, Kaiga	4.1 ± 0.9	—	[3.130]
Sacred fig tree	India	Tropical forest, Kaiga	12.9 ± 2.0	—	[3.130]
Malabar ebony	—	Tropical forest, Kaiga	13.2 ± 1.6	—	[3.130]
Shrub leaves					
Dillenia	India	Tropical forest, Kaiga	2.1 ± 1.1	—	[3.130]
Clerodendrum	India	Tropical forest, Kaiga	4.6 ± 1.1	—	[3.130]
Microcos	India	Tropical forest, Kaiga	3.6 ± 1.0	—	[3.130]
Ukshi	India	Tropical forest, Kaiga	3.4 ± 1.0	—	[3.130]
Siam weed	India	Tropical forest, Kaiga	7.6 ± 1.5	—	[3.130]
Aloe leafed cymbidium	India	Tropical forest, Kaiga	DL–4.3	—	[3.130]

[a] Values with no conversion factor in TRS 310 or TRS 472 are presented in fresh weight

[b] Geometric mean;

[c] Geometric mean / standard deviation.

— = no data available

The data in Table 3.11 demonstrate that the concentration of Ra in the bark or stem of a given plant is normally higher than that in its leaves. Most likely this is due to continuous accumulation of ^{226}Ra through root uptake [3.130]. A decreasing gradient from oldest to youngest tissues and towards the apex of the plant has also been observed for Ra transfer from roots to stems and from stems to shoots in many plant species growing at various locations with different environmental properties [3.136]. In particular, Markose et al. [3.137] have reported a geometric mean of 0.61 for the ratio of concentrations in leaves and stems. Similar ratios for different tropical forest plant species are found to vary from 0.42 to 0.84 with a mean value of 0.66 [3.130]. According to Simon and Ibrahim [3.136], these data suggest that Ra is not metabolically active and is not secondarily distributed among plant tissues.

Concentrations of ^{226}Ra in cereals and vegetables vary from values below detection limit in some vegetable samples to 2.5 Bq/kg (DW), depending on Ra concentrations in and properties of the soil, on the ability of plants to accumulate Ra, and on environmental characteristics governing the external contamination of plants. In particular, high Ra concentrations in beans are in agreement with Vasconcellos et al. [3.138], who found the highest concentration of Ra in the species that contain the elevated Ca concentration, namely beans or leguminous vegetables.

More specific data for different vegetable and fruit species obtained near Rio de Janeiro and in surrounding states are given in Table 3.12 (adapted from Ref. [3.119]).

TABLE 3.12. Ra ISOTOPE CONCENTRATIONS IN THE VEGETABLES CONSUMED GROWN IN RIO DE JANEIRO AREA

Species	*N*	^{226}Ra (Bq/kg, FW)		^{228}Ra (Bq/kg, FW)	
		GM	Range	GM	Range
Apple	3	0.035	0.010–0.100	0.067	0.010–0.310
Banana	2	0.017	0.015–0.019	0.018	0.017–0.020
Black bean	4	0.131	0.034–0.300	0.26	0.064–0.750
Cabbage	4	0.137	0.05–0.28	0.3	0.130–0.670
Carrot	3	0.146	0.064–0.250	0.69	0.597–0.930

TABLE 3.12. Ra ISOTOPE CONCENTRATIONS IN THE VEGETABLES CONSUMED GROWN IN RIO DE JANEIRO AREA (cont.)

Species	*N*	^{226}Ra (Bq/kg, FW)		^{228}Ra (Bq/kg, FW)	
		GM	Range	GM	Range
Cassava	4	0.057	0.028–0.280	0.25	0.148–0.440
Cauliflower	3	0.143	0.054–0.650	0.12	0.078–0.260
Chayote	3	0.020	0.0034–0.079	0.060	0.022–0.110
Kale	6	0.068	0.012–0.805	0.4	0.022–2.370
Lettuce	4	0.07	0.033–0.210	0.089	0.041–0.200
Onion	4	0.065	0.0066–0.650	0.11	0.0088–0.660
Orange	2	0.021	0.010–0.045	0.04	0.025–0.092
Papaya	1	0.050	—	0.17	—
Potato	3	0.023	0.012–0.054	0.081	0.046–0.125
Pineapple	1	0.024	—	0.017	—
Pumpkin	2	0.032	0.028–0.038	0.11	0.094–0.130
Spinach	6	0.03	0.010–0.097	0.21	0.084–0.430
Tomato	4	0.157	0.059–0.570	0.16	0.051–0.450
Water cress	3	0.038	0.015–0.065	0.066	0.022–0.160

— = no data available

The highest activity concentrations are in black bean, cabbage, cauliflower, carrot and tomato, (0.131–0.157 Bq/kg, FW) followed by papaya, cassava, onion, kale and lettuce (0.05–0.07 Bq/kg, FW) and, finally, fruit species, potato, spinach and water cress (0.01–0.04 Bq/kg, FW). Tracy et al. [3.139], in a study of gardens contaminated by U process effluents in Ontario, Canada, reported similar data indicating that the highest Ra concentrations were in roots and leafy vegetables. Fruits generally displayed the lowest Ra concentrations.

In most species, the activity concentration ratios of ^{228}Ra in plants were higher than those of ^{226}Ra, indicating that the concentrations of ^{228}Ra in Brazilian soil are higher than those of ^{226}Ra, which had been observed by Linsalata et al. [3.140].

Farming systems used today can be classified as conventional, organic and hydroponic. The low contribution of radionuclides to soil by fertilization was mentioned in a review by Mortvedt [3.141], who reported an annual Ra increase of 0.04% due to phosphate fertilization in tilled agricultural soils in Sweden. The data for winter wheat grain obtained in various farming systems are given in Table 3.13 [3.127], while Table 3.14 [3.142] presents similar data for vegetables. It can be seen from these data that depending on the farming practice concentrations of Ra in yield can vary by a factor of three.

TABLE 3.13. CONCENTRATIONS ^{226}Ra AND ^{228}Ra IN WINTER WHEAT PRODUCED UNDER THE DIFFERENT FARMING MANAGEMENT SYSTEMS (BQ/KG, DW)

Site	Crop management	Year	^{226}Ra	^{228}Ra
Marche-en-Famenne	Organic	2006	0. 089 ± 0.016	0.15 ± 0.06
Ciney	Organic	2006	0.078 ± 0.01	0.11 ± 0.1
Ciney	Conventional	2006	0.055 ± 0.01	0.08 ± 0.05
Ciney	Conventional	2007	0.074 ± 0.022	0.23 ± 0.14
Marche-en-Famenne	Conventional	2006	0.06 ± 0.01	0.06 ± 0.04
Marche-en-Famenne	Organic	2007	0.12 ± 0.023	0.17 ± 0.06
Marche-en-Famenne	Conventional	2007	0.21 ± 0.02	0.23 ± 0.05
Soignies	Organic	2006	0.17 ± 0.02	0.18 ± 0.05
Soignies	Conventional	2006	0.09 ± 0.01	0.12 ± 0.04
Soignies	Organic	2007	0.09 ± 0.02	0.13 ± 0.04
Soignies	Conventional	2007	0.09 ± 0.02	0.16 ± 0.05

TABLE 3.14. CONCENTRATIONS ^{226}Ra AND ^{228}Ra IN VEGETABLES FOR THE DIFFERENT TYPES OF FARMING MANAGEMENT (BQ/KG, DW)

Vegetable	Crop management	N	^{226}Ra			^{228}Ra		
			GM	GSD	Range	GM	GSD	Range
Black beans	Conventional	6	1.4	1.3	1.0–2.0	2.4	1.2	2.0–2.9
	Organic	6	1.48	1.30	1.02–2.0	2.3	1.2	1.7–3.0
Lettuce	Conventional	4	1.54	1.54	1.0–2.8	2.4	1.8	1.3–4.9
	Organic	4	1.38	1.83	0.7–2.4	2.5	2.4	0.9–7.5
	Hydroponic	4	0.51	1.45	0.32–0.77	0.6	2.7	0.1–0.95
Carrots	Conventional	4	2.19	1.78	1.14–3.4	2.6	2.1	1.1–4.8
	Organic	5	2.39	1.46	1.37–4.2	5.5	1.4	4.0–8.1

Observations on low Ra mobility in woody plants are also found to be valid for cereals and grassy plants. Pulhani et al. [3.126] reported that about 50% of total ^{226}Ra is seen to accumulate in the roots and about 22% in the shoots and husk, following a decreasing pattern of root > shoot > husk > grain. Similar data presented by Lindahl et al. [3.127] also show that the highest concentrations of Ra isotopes are found in the roots, followed by the stem (approximately 3–5 times lower than in the roots), while the lowest concentrations (more than ten fold lower than in the roots) were found to be in the grain.

The data presented in this section also demonstrate that the corresponding ^{228}Ra values are somewhat higher than those for ^{226}Ra in the same plants (tissues). However, it is important to realize that this ratio depends on concentrations of ^{226}Ra and ^{228}Ra in soil which can vary across a wide range contaiminating plants with different contributions of Ra isotopes.

As mentioned earlier, there are some areas around the world where activity concentrations of Ra in the soil are several orders of magnitude higher than average worldwide values. Therefore, corresponding concentrations of Ra in plants and animals in areas of high natural background radiation can also be much higher than those given in Table 3.11. Therefore, such areas are a subject of extended radiological monitoring and much information on plant contamination was obtained to assess radiological conditions within such territories. Therefore, only some typical examples of contamination of plants grown in areas of high background radiation are given in Table 3.15 [3.3, 3.129, 3.143].

TABLE 3.15. Ra-226 ACTIVITY CONCENTRATIONS IN PLANTS (AREAS OF HIGH BACKGROUND RADIATION) IN BQ/KG (DW)

Group of plants	Country	Region	^{226}Ra	Reference
Cereals (rice)	India	Chavara, Kerala	DL[a] – 0.779	[3.3]
Fruits	Germany	Black Forest	0.74–56.9	[3.3]
Fruits (papaya)	India	Tamil Nadu	DL[a]–5.31	[3.3]
Fruits[d]	Islamic Republic of Iran	Ramsar	53.8–1449[b]	[3.3]
Grass	Russian Federation	Komi	770 ± 482	[3.129]
Grass (hay)	Germany	Black Forest	30.1–2151	[3.3]
Grass	Russian Federation	Komi	33.5–2064.5	[3.143]
Leafy vegetables	India	Tamil Nadu	3.68–23.7	[3.3]
Other vegetables	India	Tamil Nadu	DL[a]–31.5	[3.3]
Tree leaves (mountain ash)	Russian Federation	Komi	291.6	[3.143]
Tree leaves (willow)	Russian Federation	Komi	176–188	[3.143]
Vegetables	Germany	Black Forest	0.24–41.3	[3.3]
Vegetables[c]	Islamic Republic of Iran	Ramsar	0.39–14.4[b]	[3.3]

[a] Detection Limit
[b] Ra-226 = 1.86–7.14 kBq/kg soil
[c] beans, tomato, garlic, etc.
[d] pomegranate, peach, orange, etc.

Overall, these data show that most of the trees, cereals, fruits and vegetables grown in high background areas have significantly higher ^{226}Ra concentrations compared to the normal areas. In particular, the mean ^{226}Ra activity concentration in grass (*Vicia grassa*) of approximately 770 ± 481 Bq/kg (FM) reported by Evseyeva [3.129] for highly contaminated sites of the Komi Republic is two orders of magnitude higher than that reported for normal areas. Because of the high inhomogeneity of these areas, ranges of concentrations of Ra in some species are much wider than those given in Table 3.14. Based on the extensive survey of the Komi region, Taskayev [3.143] gave a range of 33.5–2064 Bq/kg (DW) for ^{226}Ru concentration in grass.

Similarly, differences of one to two orders of magnitude were also found for other plants such as woody plants (trees), vegetables, cereals and nuts. However, because of high inhomogeneity in ^{226}Ra concentrations in soils of both normal areas and areas of high radiation background, some of the plant samples taken in areas of high background radiation tend to exhibit low Ra isotope concentrations, comparable with those found in normal background areas, whereas some samples tend to show high Ra concentrations in plants. Thus, concentrations of Ra in papaya fruits varied from the detection limit to 0.23 Bq/kg (DW) in the Bombay area, while in Tamil Nadu (high background radiation area) this range was from the detection limit to 5.31 Bq/kg (DW).

Most data in the literature on plant Ra concentrations pertain to ^{226}Ra; few data are available for ^{228}Ra and ^{224}Ra; thus, unless otherwise stated, the values presented pertain to ^{226}Ra. Simon and Ibrahim [3.136] reviewed the literature on Ra concentration in plants. Tabulated plant concentrations for natural environments varied from 0.0044 to 52 Bq/kg (DW). The highest concentrations were observed for the Brazil nut followed by tobacco; lichens and mosses also tend to concentrate Ra. The high values (from 30 to 52 Bq/kg) observed by Penna Franca et al. [3.144] for the Brazil nut tree were found for high background areas in the Amazon Valley. They also observed that the tree has high Ba concentrations. This suggests that Ba is functioning as a carrier for Ra. From a recent survey of radionuclide activity concentrations in biota in the UK [3.145], activity concentrations in grasses ranged from 0.037 to 1.7 Bq/kg fresh weight for grasses and from 0.0046 to 0.18 Bq/kg fresh weight for pine.

Concentrations observed in plants and edible crops in high natural background areas tend to be much higher, ranging from 0.1 to 5.1 × 10^4 Bq/kg (DW) [3.136]. High values were for example observed in a New Zealand uraniferous area (2.0 × 10^2–5.1 × 10^4 Bq/kg, [3.146]), in an area of Iran high in natural Ra (7−190 Bq/kg; [3.147]), and in the fomer Soviet Union in areas contaminated via migration of natural radiation (630−15 900 Bq/kg ash [3.148, 3.149]). Recent studies confirm earlier findings. Changizi et al. [3.150] monitored ^{226}Ra and ^{228}Ra concentrations for parsley and leek in the Tehran high background area and found concentrations for parsley of 177 and 349 Bq/kg FW for ^{226}Ra and ^{228}Ra, respectively and for leeks, values of 9.4 and 226 Bq/kg FW, respectively. Shanthi et al. [3.151] monitored ^{226}Ra concentrations in a number of vegetables grown in the high natural background areas of southwestern India and recorded values from 0.1 to 5 Bq/kg. Alder leaf concentrations sampled at a distance of 8 to 400 m from the top of a U mine heap located in the Yakutia area ranged from 55 to 555 Bq/kg ash weight (soil concentrations from 22–10545 Bq/kg) [3.152]. The plant concentrations in high natural background areas as summarized by Simon and Ibrahim [3.136] were generally higher than those observed on U tailings (ranging from 0.014–3100 Bq/kg). In the case of sulphuric acid leached tailings, this may be due to the presence of Ra mainly as sulphate. Radium sulphate is extremely stable [3.153] with low solubility, which explains the lower uptake.

Some of the best evidence for high concentrations of ^{228}Ra in plants in areas of high background radiation has been reported by Iyengar [3.3]. Detailed investigations of 30 plant species of 18 families in the areas of Kerala and Tamil Nadu showed activities of 1490 Bq/kg (DW) for ^{228}Ra (from ^{228}Th) and 2170 Bq/kg (DW) for ^{224}Ra, while the plant *Crotalaria retusa* showed the least activity. These studies have conclusively demonstrated that ^{228}Ra may be the main long lived radionuclide absorbed by plants growing in monazite bearing high background areas. The extent of this absorption by plants depends upon the radionuclide concentration in the soil, as well as the nature of the root system and growth pattern of the plant species.

The data show that in some of the leafy vegetables, ^{228}Ra concentrations are higher by a factor of 5 as compared with values measured in areas of normal radiation background. Values by region show that Guarapari appears to have relatively lower Ra concentrations in leafy vegetables when compared with Araxa. This may be due to the low solubility of the monazite present in Guarapari, leading to reduced uptake by the plant, while in Araxa the apatite association with radioactive minerals in the area enriches the Ra content in many crop categories. Some of the highest values have been noticed in fruits, leafy vegetables and kidney beans.

3.8. RADIUM IN TERRESTRIAL ANIMALS

The major pathway for Ra transfer to animals is through ingestion of feed and water [3.3]. However, Ra concentrations in food and water can vary considerably even within a limited geographical location. In addition, there are seasonal variations in both Ra concentrations in plants and in the diet patterns of animals which have a bearing on Ra incorporation in animals. All these factors lead to high variations in Ra intake by animals and Ra concentrations in different animal tissues.

Radium metabolism in animals qualitatively follows Ca to a large extent, being deposited in areas prone to calcium accretion [3.3]. However, it has also been observed that there is some discrimination between Ra and Ca in some tissues, such as bone [3.51].

A summary of the data on ^{226}Ra distribution among different tissues of cattle and pig, mainly adapted from the review by Iyengar [3.3], is given in Table 3.16. The regions for which data are presented in Table 3.13 can be considered to be areas of normal radiation background.

TABLE 3.16. Ra-226 IN AGRICULTURAL ANIMALS IN NORMAL AREAS

Animal	Tissues	Country	^{226}Ra (Bq/kg, FW)
Cattle	Muscles	Germany	0.03
	Blood	Germany	0.007
	Teeth	Germany	6.22 – 64.2
	Bone	Germany	4.5–22.5
	Soft tissues	Russian Federation	0.04–0.07
	Bones	Russian Federation	3.7–4.4
	Soft tissue	USA	0.0004
	Bone	USA	0.002–0.30
Pig	Muscles	Germany	0.03–0.06
	Liver	Germany	0.03
	Muscles	USA	0.0005–0.004
	Bone	USA	0.5–1.1
	Blood	USA	0.002–0.0046
	Lung	USA	0.0074–0.012
	Liver	USA	0.0005–0.005
	Kidney	USA	0.0012–0.0067

Radium-226 activity concentrations in cattle muscles (or soft tissues) are generally very low compared to those in teeth and bones presented in the same source [3.154]. Pig data display a similar contamination pattern. Radium concentrations in pig muscles, as well as in other soft tissues (the liver, heart and kidney) are lower than that in bone. Among offal and muscles, the highest Ra concentrations are found to be in the lung, while Ra in the blood is found within a narrow range, (0.0019–0.0044 Bq/kg FW), which shows the soluble Ra to be in a state of migration to different body tissues [3.3].

Although data on Ra in game are rather scarce, there are several information sources which provide data for various wild animals and birds from temperate and arctic environments (Table 3.17 [3.115], Table 3.18 [3.155, 3.156], Table 3.19 [3.148] and Table 3.20 [3.19, 3.156]).

TABLE 3.17. Ra-226 IN BIG GAME OBTAINED FOR TEMPERATE CONDITIONS IN EUROPE

Game	Tissue	^{226}Ra (Bq/kg, FW)
Deer[a]	Muscle	0.18–0.95
	Bone	2.6–12.0
Buck[a]	Muscle	0.41
	Bone	14.8
	Hooves	8.4
	Antlers	44.4
Wild boar	Muscle	0.86
	Bone	14.7
Chamois[b]	Muscle	0.049
Bear	Muscle	0.41–0.47
	Bone	2.1–15.0

[a] Authors have not specified the units used, i.e. whether the results reported are in wet weight, dry weight or ash weight

TABLE 3.18. Ra-226 IN ARCTIC ANIMALS

Game	Tissue	Region/country	^{226}Ra (Bq/kg, FW)	References
Caribou	Muscle	Canada	0.054	[3.155]
	Bone	Canada	8.33	[3.155]
Reindeer	Muscle	Canada	0.011	[3.155]
	Bone	Canada	13.5	[3.155]
	Whole body	Komi, Russian Federation	0.22	[3.156]
Elk/Moose	Muscle	Canada	0.015	[3.155]
	Bone	Canada	3.24	[3.155]
	Whole body	Komi, Russian Federation	0.19	[3.156]

In particular, data for ^{226}Ra concentrations in large wild animals from temperate forests (bear, deer, buck, wild boar, chamois) were presented by Kljaic et al. [3.115] (Table 3.17), while Taskayev and Testov [3.156] and Holtzman [3.155] reported data on Ra concentrations in the large animals of the Arctic tundra: caribou, reindeer and elk/moose (Table 3.18). As was observed for domestic animals (see Table 3.16), the highest concentrations (2.1–44.4 Bq/kg) were found in bone, especially in antlers (up to 44.4 Bq/kg). Concentrations of Ra in muscle and in bone followed a similar pattern for both temperate animals and for Arctic species: the concentration of Ra in muscles was between one and three orders of magnitude lower compared to the concentration in bone.

Some differences were also observed between animals from temperate and from Arctic areas. Thus, the data from Europe (Table 3.17) show that ^{226}Ra concentrations in muscle in all of the animals are higher than those observed in the Arctic and vary within a narrow range. The bones of the animals, while having higher ^{226}Ra concentrations than muscles , show a wide range, e.g. bear bones: 2.1–15.0 Bq/kg and deer bones: 2.6–12.0 Bq/kg. In the case of buck, ^{226}Ra in bone registers a value of 14.8 Bq/kg. The highest value of 44.4 Bq/kg has been recorded for antlers. In addition, the data obtained for Arctic animals in various continents, although given for different tissues, seem to follow the same tendency. Data reported for tundra in the Russian Federation by Taskayev and Testov [3.156] for whole animal bodies (0.19–0.22 Bq/kg) are between

^{226}Ra concentrations in muscles and bones, presented by Holtzman [3.155] for Canadian tundra.

The accumulation of ^{226}Ra in various biota species was a subject of many long term comparative studies carried out in areas with differing radiation background located in the Komi Republic of the Russian Federation [3.19, 3.148, 3.156]. These studies are presented in Tables 3.19 (adapted from Ref. [3.148]) and 3.20. In particular, Ref. [3.148] gives age dependent data on Ra concentrations in small rodents (the tundra vole) (Table 3.19).

TABLE 3.19. RADIUM CONCENTRATIONS IN THE TISSUES OF SMALL RODENTS, *MICROTUS OECONOMUS*

Type of area	^{226}Ra conc. in soil, Bq/kg(DW)	^{226}Radium conc. in animal, Bq/kg (DW)			
		<2 months	2–6 months	6–12 months	12–18 months
High activity area	26 300	1570	2790	5570	5550
Average activity area	1110	625	700	1370	1460
Low activity area	170	250	300	340	370
Control area	30	15	21	22	24

The data demonstrate that the Ra concentrations in the animals are age dependent. In particular, a clear increase in the ^{226}Ra content in mammals up to 12 months old is noted. The subsequent growth period, i.e. 12–18 months, shows a very marginal rise in ^{226}Ra content. This trend is uniform in all three activity plots studied, as is a control area. These findings are supported by the data reported by Muth et al. [3.51] for old chickens showing that at the end of the bone growth period (60–100 days), the specific bone activity remained steady.

A summary of the research on areas of differing radiation background was reported by Taskayev and Testov [3.156]. The data presented in Table 3.20 [3.19, 3.156] show quite high variations among the species studied. However, the whole body ^{226}Ra concentrations in all the studied species were rather low even in areas of high background radiation, although they were still up to one order of magnitude higher than values observed in normal areas.

TABLE 3.20. CONCENTRATIONS OF ^{226}Ra IN WILDLIFE SPECIES IN AREAS OF THE KOMI REPUBLIC, RUSSIAN FEDERATION, WITH DIFFERENT RADIATION BACKGROUNDS

Biota Species	Normal areas		Areas of high background radiation	
	n	^{226}Ra (Bq/kg, FW)	*n*	^{226}Ra (Bq/kg, FW)
Small rodents	862	1.1 ± 0.4	309	8.6 ± 1.6
Mole (*Talpa europaea*)	36	1.81	49	12.2
Shrew (*Sorex arraneus* Linn.)	94	0.59	56	9.2
Tundra vole *(Microtus oeconomus* Pall.*)*	491	1.3	38	8.5
Dark vole (*Microtus agrestis*)	68	1.3	7	7.4
Redhead vole *(Myodes glareolus)*	46	0.96	74	8.9
Water vole (*Arvicola terrestris*)	39	0.89	11	7.4
Red vole (*Clethrionomys rutilus* Pall.)	49	0.92	63	7.8
Bank vole (*Myodes glareolus*)	39	0.89	11	7.4
Small herbivorous animals	45	0.3 ± 0.13	55	4.6 ± 1.7
Squirrels (*Sciurus*)	15	0.15	36	2.2
Chipmunks (*Tamias)*	18	0.33	5	4.4
Hare (*Lepus timidus*)	12	0.41	14	5.6
Small carnivorous animals	44	0.53 ± 0.15	44	4.6 ± 2.1
Marten (*Martes)*	12	0.41	8	6.7
Ermine (*Mustela erminea*)	13	0.7	9	5.9
Weasel (*Mustela nivalis*)	5	0.7	10	6.6
European mink (*Mustela lutreola)*	5	0.56	5	3.3
Otter (*Lutra lutra*)	6	0.52	9	3.3
Fox (*Vulpes Vulpes*)	3	0.3	3	1.8

TABLE 3.20. CONCENTRATIONS OF ^{226}Ra IN WILDLIFE SPECIES IN AREAS OF THE KOMI REPUBLIC, RUSSIAN FEDERATION, WITH DIFFERENT RADIATION BACKGROUNDS (cont.)

Biota Species	Normal areas		Areas of high background radiation	
	n	^{226}Ra (Bq/kg, FW)	*n*	^{226}Ra (Bq/kg, FW)
Amphibian and Reptiles		*0.37–0.44*		
Viviparous lizard *(Zootoca vivipara)*	57	0.37		
Moor frog (*Rana arvalis*)	31	0.44	19	7.0
Herbivorous and insectivorous birds	195	0.5 ± 0.35	818	
Western capercaillie *(Tetrao urogallus*)	17	0.74	205	6.5
Black grouse *(Lyrurus tetrix)*	15	0.96	184	6.9
Hazel grouse *(Tetrastes bonasia)*	25	0.37	208	4.3
Willow grouse *(Lagopus lagopus)*)	15	0.63	61	3.2
Eurasian teal (*Anas crecca*)	7	1.1	5	13.0
Eurasian wigeon (*Anas penelope*)	3	0.92		
Goosander (*Mergus merganser*)	4	0.78	4	13.7
Siberian jay (*Perisoreus infaustus)*	28	0.19	41	0.7
Common crossbill (*Loxia curvirostra)*	30	0.19	12	0.4
Parrot crossbill (*Loxia pytyopsittacus)*	18	0.19	41	0.4
Great tit (*Parus major*)	15	0.15	19	0.3
White wagtail (*Motacilla alba)*	12	0.19	21	0.3
Bullfinch (*Pyrrhula pyrrhula*)	6	0.15	17	0.2
Woodpeckers	69	0.37	16	3.3–4.4
Greater spotted woodpecker *(Dendrocopos major)*	12	0.37	6	3.3

TABLE 3.20. CONCENTRATIONS OF ^{226}Ra IN WILDLIFE SPECIES IN AREAS OF THE KOMI REPUBLIC, RUSSIAN FEDERATION, WITH DIFFERENT RADIATION BACKGROUNDS (cont.)

Biota Species	Normal areas		Areas of high background radiation	
	n	^{226}Ra (Bq/kg, FW)	*n*	^{226}Ra (Bq/kg, FW)
Woodpecker *(Dryocopus martius)*	57	0.37	10	4.4
Carnivorous birds	11	0.71 ± 0.43	13	6.3 ± 5.8
Goshawk (*Accipiter gentilis*)	2	0.3	3	1.22
Sparrow-hawk (*Accipiter castanilius*)	3	0.37	4	1.41
Eurasian eagle-owl (*Bubo bubo*)	2	1.1	3	11.1
Ural Owl (Strix uralensis)	4	1.07	3	11.5

The highest concentrations of Ra were found to be in insectivorous (mole and shrew) and various mouse rodent species, while the lowest values were observed in herbivorous rodents, such as squirrels.

Among birds, elevated concentrations of Ra were found in owl, waterfowl and grouse species. The lowest concentrations are specific to herbivorous species of the passerine family. Diurnal birds of prey occupy an intermediate position in terms of Ra accumulation.

It is important to mention that the whole body data above are given without consideration of the ^{226}Ra concentrations in the craw and gizzard. High internal contamination of the gizzard has been noted in some studies [3.157]. In particular, research in the high background areas of Kerala, India, showed that fowl had very high ^{228}Ra concentrations in their gizzards (35.5–540 Bq/kg). The ^{228}Ra concentrations in other organs were much lower: 0.37–3.33 Bq/kg in muscles, 44.4–68.5 Bq/kg in bones and 56.2 Bq/kg in eggshell. The high concentration of Ra in the gizzard was attributed to the pecking habit of fowl feeding in the area, leading to the ingestion of radioactive sand along with their feed [3.3].

Overall, the data on ^{226}Ra concentrations in different biota species reflect their specific consumption habits and the position of every species in the trophic chain. In particular, based on the data obtained for both normal areas and areas of high background radiation, the concentration of Ra in various biota species can be presented as the descending sequence: insectivores (soil animals) > mice rodent species > carnivores > ungulates.

3.9. RADIUM IN FRESHWATER BIOTA SPECIES

Freshwater biota show an appreciable potential for accumulating Ra in a range of environments (Table 3.21, from Refs [3.3, 3.158]). For instance, the algae *Spirogyra* sp. exhibit good accumulation of ^{226}Ra, and could therefore serve as a highly useful indicator species for environmental Ra. Other biota species, such as mussels, fish and aquatic macrophytes, also appear to possess qualities that make them suitable for use in monitoring.

As mentioned earlier, Ra can be present in the water in a very wide range of concentrations. The concentration of ^{226}Ra has been investigated both in regions with a high natural occurrence of Ra and in places where anthropogenic activities, such as mineral mining and the processing of wastes, result in water pollution. These places are mainly in regions where U ore is mined and treated, such as in Australia, Canada, Bosnia and Herzegovina, Croatia, the Czech Republic, France, India, Japan, Serbia, Slovakia, and the United States of America.

TABLE 3.21. RADIUM ISOTOPE CONCENTRATIONS IN FRESHWATER BIOTA

Country/location	Biota	^{226}Ra (Bq/kg, WW)
Belgium/Tessenderlo,	Plankton (mixed)	2780
India/Jaduguda,	Stream algae	251–8930
USA/Hudson River,	Zooplankton (*Gammarus* sp.)	
	(a) Whole body	1.74
	(b) GI tract	19.1
	(c) Soft tissue	0.17
	(d) Unidentified organ	13.4
	(e) Exoskeleton	0.67
	(f) Appendages	0.27
USA/Animas	Stream algae	168 (2.52 Bq/kg ash)
	Stream algae	2200

TABLE 3.21. RADIUM ISOTOPE CONCENTRATIONS IN FRESHWATER BIOTA (cont.)

Country/location	Biota	^{226}Ra (Bq/kg, WW)
Canada/Saskatchewan	Aquatic macrophytes	
	Background area	1.44
	Drill area	72.2
Australia/Alligator Rivers	Freshwater mussels	1.1–166
Australia	Barramundi, soft parts	0.19–8.51
	Barramundi, soft parts	0.37–13.0
	Black bream, soft parts	2.96–3.7
	Black bream, soft parts	2.96–3.7
Canada	Northern pike	0.11
	Longnose sucker	0.074
	White sucker	0.185
	Arctic grayling	0.63
Czech Republic	*Anguilla anguilla* Linn.	5.6–12.6
Belgium	Bream, soft tissue (eviscerated whole)	7.62
	Barbel, soft tissue (eviscerated whole)	1.77
	Trout, soft tissue (eviscerated whole)	2.83
India/Alwaye	*Ophiocephalus sp.*	
	(a) Soft tissue	<0.074
	(b) Bone	0.703
	Clupea longiceps	
	(a) Soft tissue	0.37
	(b) Bone	0.89
	Etroplus	
	(a) Soft tissue	0.15–0.24
	(b) Bone	4.26–8.54

TABLE 3.21. RADIUM ISOTOPE CONCENTRATIONS IN FRESHWATER BIOTA (cont.)

Country/location	Biota	^{226}Ra (Bq/kg, WW)
India/Jadugada	*Catla catla*	
	(a) Soft tissue	0.2
	(b) Bone	13.0
	Labeo rohita	
	(a) Soft tissue	0.019
	(b) Bone	0.55
	Ophiocephalus sp.	
	(a) Soft tissue	2.6–7.9
	(b) Bone	20.6–40.0
Italy	Lake fish	0.052–0.12
Former Yugoslavia	Various species	0.05–1.67
	Fish from mine water drains	
	(a) Soft tissue	2.96
	(b) Bone	51.8

The general trend is that higher freshwater Ra concentrations equate to elevated Ra concentrations in biota. Table 3.22 [3.156] provides an example of increased Ra concentration in fish in areas of high background radiation as compared to normal areas. Similarly, Table 3.23 [3.69, 3.70, 3.159–3.173] shows that ^{226}Ra concentration in primary producer vegetation is higher in contaminated sites than in reference sites.

In Table 3.24 [3.60, 3.64, 3.65, 3.67–3.71, 3.160–3.162, 3.167–3.191], the ^{226}Ra content in fish (whole body) living in uncontaminated surface water ranges from 0.68 to 1.12 Bq/kg (fresh weight). In surface water affected by U milling, the ^{226}Ra content in fish ranges from 0.33 to 10.4 Bq/kg (fresh weight). Comparison of Ra activity concentrations in bone relative to muscle indicate that in exposure areas, Ra tends to be higher in bone than muscle, whereas in reference areas, this trend does not consistently hold.

TABLE 3.22. SUMMARY OF DATA ON ^{226}Ra IN FISH IN AREAS OF THE KOMI REPUBLIC, RUSSIAN FEDERATION, WITH DIFFERENT RADIATION BACKGROUNDS

Biota species	Normal areas		Areas of high background radiation	
	n	^{226}Ra (Bq/kg)	*n*	^{226}Ra (Bq/kg)
Grayling *(Thymallus thymallus)*	15	1.1	18	3.3
Burbot (*Lota lota*)	5	2.4	5	25.9
Atlantic Salmon (*Salmo salar*)	15	1.1	15	3.3

TABLE 3.23. RADIUM-226 ACTIVITY CONCENTRATIONS IN TISSUES OF PRIMARY PRODUCERS FROM REFERENCE AND EXPOSURE SITES IN SASKATCHEWAN, CANADA

Species	Type of habitat	Ra-226 activity concentration (Bq/kg, FW)			Reference
		Mean	*N*	SD	
Reference sites					
Pondweed	Freshwater	3.46×10^{1}	6	1.58×10^{1}	[3.159]
Yellow pond lily	Freshwater	2.57×10^{1}	35	9.65	[3.160]
Common cattail	Wetland	1.36×10^{1}	6	1.53×10^{1}	[3.161]
Labrador Tea	Wetland	2.13×10^{1}	90	4.85×10^{1}	[3.160, 3.162–3.164]
Sedge	Wetland	6.97	193	3.35	[3.159, 3.165, 3.166]
Black spruce	Wetland	1.08×10^{2}	3	1.18×10^{1}	[3.70]
Blueberry	Terrestrial	7.88	72	2.35	[3.162–3.164]
Lichen	Terrestrial	2.86	66	3.68×10^{-1}	[3.162–3.164, 3.167]
Willow	Terrestrial	1.74×10^{2}	3	8.58×10^{1}	[3.163, 3.164]

TABLE 3.23. RADIUM-226 ACTIVITY CONCENTRATIONS IN TISSUES OF PRIMARY PRODUCERS FROM REFERENCE AND EXPOSURE SITES IN SASKATCHEWAN, CANADA (cont.)

Species	Type of habitat	Ra-226 activity concentration (Bq/kg, FW)			Reference
		Mean	*N*	SD	
Exposure sites					
Richardson's pondweed	Freshwater	4.90×10^1	19	2.97×10^1	[3.159]
Yellow pond lily	Freshwater	1.55×10^1	99	9.44	[3.162, 3.168]
Common cattail	Wetland	9.92×10^1	110	2.03×10^2	[3.70, 3.161, 3.169]
Labrador tea	Wetland	4.51×10^1	279	1.02×10^2	[3.160, 3.162–3.164]
Sedge	Wetland	2.51×10^1	282	7.53×10^1	[3.159, 3.165, 3.170–3.172]
Water sedge	Wetland	9.28×10^2	1	—	[3.70]
Black spruce	Wetland	3.01×10^2	3	2.77×10^2	[3.69]
Blueberry	Terrestrial	3.05×10^1	273	6.22×10^1	[3.160, 3.162–3.164]
Foxtail barley	Terrestrial	1.82×10^3	10	2.88×10^3	[3.161]
Grass	Terrestrial	1.94×10^3	9	2.46×10^3	[3.69]
Reindeer lichen	Terrestrial	5.50×10^1	252	1.04×10^1	[3.161–3.164, 3.168, 3.173]
Willow	Terrestrial	1.42×10^1	3	3.34	[3.69]

— = no data available

TABLE 3.24. RADIUM-226 ACTIVITY CONCENTRATIONS IN TISSUES FROM FRESHWATER FISHES FROM REFERENCE AND EXPOSURE SITES IN CANADA

Region	Species	Tissue type	Ra-223 Activity Conentration			Reference
			Mean	*N*	SD	
Reference sites						
Ontario	Lake whitefish	Bone	5.04	2	7.01	[3.174]
Ontario	Lake whitefish	Muscle	9.68	2	1.32×10^{1}	
Saskatchewan	Lake whitefish	Bone	9.33	111	3.86×10^{1}	[3.68–3.70, 3.175–3.177]
Saskatchewan	Lake whitefish	Muscle	4.71×10^{-1}	123	8.49×10^{1}	
Saskatchewan	Lake whitefish	Whole body	6.84×10^{-1}	148	6.52×10^{-1}	
Ontario	Lake trout	Bone	7.32	2	4.46	[3.174]
Ontario	Lake trout	Muscle	9.40	2	1.32	
Saskatchewan	Northern pike	Bone	2.14	111	1.29	[3.160, 3.162]
Saskatchewan	Northern pike	Muscle	1.41×10^{-1}	81	6.67×10^{2}	[3.59, 3.167, 3.172, 3.175, 3.178, 3.180]
Saskatchewan	Northern pike	Whole body	1.12	145	5.85	
Exposure sites						
Saskatchewan	Lake chub	Whole body	1.04×10^{1}	44	4.08×10^{1}	[3.68–3.70]
Ontario	Lake whitefish	Bone	1.23×10^{1}	3	5.13	[3.174]
Ontario	Lake whitefish	Muscle	2.10×10^{1}	3	1.65×10^{1}	
Saskatchewan	Lake whitefish	Bone	3.94	151	7.12	[3.60, 3.65, 3.68, 3.170, 3.180,]
Saskatchewan	Lake whitefish	Muscle	1.55×10^{-1}	143	1.78×10^{-1}	
Saskatchewan	Lake whitefish	Whole body	2.92	271	1.88×10^{1}	
Saskatchewan	Longnose sucker	Bone	1.30	26	6.84×10^{-1}	[3.68]
Saskatchewan	Longnose sucker	Muscle	1.06×10^{-1}	28	4.76×10^{-2}	
Saskatchewan	Longnose sucker	Whole body	3.33×10^{-1}	32	2.86×10^{-1}	
Saskatchewan	White sucker	Bone	1.26×10^{1}	131	2.93×10^{1}	[3.59, 3.63, 3.64, 3.673.167, 3.175]
Saskatchewan	White sucker	Muscle	5.53×10^{-1}	135	1.21	
Saskatchewan	White sucker	Whole body	2.86	213	5.90	
Ontario	Lake trout	Bone	9.25	4	6.13	[3.174]

TABLE 3.24. RADIUM-226 ACTIVITY CONCENTRATIONS IN TISSUES FROM FRESHWATER FISHES FROM REFERENCE AND EXPOSURE SITES IN CANADA (cont.)

Region	Species	Tissue type	Ra-223 Activity Conentration			Reference
			Mean	*N*	SD	
Ontario	Lake trout	Muscle	2.98×10^{1}	4	4.16×10^{1}	[3.174]
Saskatchewan	Lake trout	Bone	7.40	10	3.31	[3.63, 3.64]
Saskatchewan	Lake trout	Muscle	3.40×10^{-1}	10	1.84×10^{-1}	
Saskatchewan	Lake trout	Whole body	1.40	20	6.34×10^{-1}	
Saskatchewan	Northern pike	Bone	2.37×10^{1}	341	6.11×10^{1}	[3.59, 3.63–3.67, 3.160, 3.167–3.172, 3.176–3.191]
Saskatchewan	Northern pike	Muscle	1.46	300	5.46	
Saskatchewan	Northern pike	Whole body	5.24	528	1.17×10^{1}	

3.10. RADIUM IN MARINE BIOTA SPECIES

3.10.1. Ra concentrations in marine biota

The current database on Ra isotopes in marine biota is very scarce. Measurement of Ra isotopes in biota is usually performed by alpha and gamma spectrometry. Most studies deal with the long lived isotope ^{226}Ra, often measured through the gamma rays of ^{214}Pb and ^{214}Bi daughters, through the ^{226}Ra alpha emission or through the measurement of the decay product ^{222}Rn. Radium-228 is usually determined through chemical separation and beta counting or through the measurement of its decay product ^{228}Th. Few data are available on ^{228}Ra and virtually none on ^{224}Ra and ^{223}Ra in biota. Most of the available data is therefore on ^{226}Ra, with limited data on ^{228}Ra.

Radium-226 activity concentrations in phytoplankton and multicellular marine algae are generally low and range between 0.05 and 1.9 Bq/kg (FW, Table 3.25 [3.192–3.197]).

TABLE 3.25. RADIUM-226 ACTIVITY CONCENTRATIONS IN ENVIRONMENTAL SAMPLES OF MULTICELLULAR ALGAE

Taxa	Macroalgae	Region	Bq/kg	Reference
Phaeophycea and Rhodophycea	5 species	North Sea	0.05–1.9	[3.192]
Phaeophycea and Cholophycea	5 species	Red Sea	(0.74–1.64)	[3.193]
Phaeophycea, Rhodophycea and Cholophycea	20 species	Caribbean Sea, Puerto Rico	(0.12–0.88)	[3.194]
Phaeophycea,	3 species	Pacific coast of Japan	(0.52–1.40)	[3.195]
Phaeophycea and Chlorophycea	2 species	Atlantic coast of Portugal	0.18–0.49	[3.196]
Phaeophycea	1 species	Bohai and Yeallow Seas of China	0.41	[3.197]

Note: Data not in parenthesis is as reported; data in parenthesis has been converted to wet weight basis assuming ratio FW:DW = 5.

Some algae species were reported to accumulate ^{226}Ra in higher concentrations, such as *Zooxanthella* associated with coral reefs, with a drinking water concentration factor of approximately 3 × 10^6. However, the mechanisms responsible for this increased accumulation have not yet been described [3.192].

Although there was significant interest in radionuclides in the marine environment, which, over several decades, triggered experimental research on the accumulation and excretion of radionuclides in biota, the interest motivated work focused mainly on artificial radionuclides present in nuclear reactor releases, with less attention paid to radionuclides of the natural decay series. For example, a vast survey of the literature in the Russian language on radioecology work reported between the late 1950s and 2008 [3.198] identified only one study on ^{226}Ra in marine fish [3.199]. In addition, most information available on Ra in marine biota comes from field surveys rather than laboratory experiments.

Radium-226 concentrations for animal species from several seas around the world are summarized in Table 3.26 [3.193-3.201] and generally fall within the same range. Radium-226 concentrations in large marine mammals and fish muscle, including common planktivorous species and large predators such as tuna and the blue marlin, are below 1 Bq/kg (WW). Common filter feeding molluscs such as mussels displayed concentrations from <0.1 to 0.3 Bq/kg (WW). The highest concentrations reported for ^{226}Ra in animal biota was 2.7 Bq/kg (WW) for edible tissues of ascidians and 24 Bq/kg (WW) for livers of ascidians.

TABLE 3.26. RADIUM-226 ACTIVITY CONCENTRATIONS IN MARINE FAUNA

Biota	Region	^{226}Ra (Bq/kg, FW)	^{228}Ra (Bq/kg FW)	Ref.
Ascidians: edible parts	Pacific Ocean, Japan	(0.34–0.54)	0.36–0.70	[3.195]
Ascidians: liver	Pacific Ocean, Japan	(0.5–5.6)	0.34–7.2	[3.195]
Barnacle	Pacific Ocean, Japan	(<2.8)	<1.52	[3.195]
Shrimp and crabs	Bohai and Yellow Seas, China	0.18 ± 0.13	—	[3.197]
Shellfish	Bohai and Yellow Seas, China	0.23 ± 0.23	—	[3.197]
Mussels	Pacific Ocean, Japan	(0.36 ± 0.06)	0.26 ± 0.02	[3.195]
Mussels	Atlantic Ocean, Portugal	<0.1–1.5 ± 0.3	—	[3.196]
Molluscs	Red Sea, Sudan	(0.87–0.89)	—	[3.193]
Fish muscle	Bohai and Yellow Seas, China	0.11 ± 0.16	—	[3.197]
Fish muscle, several species	NE Atlantic	0.4–0.6	—	[3.200]
Fish muscle several species	NW Atlantic (Iceland and Labrador Seas)	0.156–0.876	—	[3.201]

Note: Data in parenthesis is as reported; other data has been converted to wet weight basis assuming ratio FW:DW = 5.

— = no data available

A compilation of data mostly pertaining to the Gulf of Mexico was summarized in Neff [3.202]. Although reported on a dry weight basis, these concentrations converted to an estimated wet weight basis are roughly similar to concentrations reported for other regions of the world. Radium-226 concentrations are on average higher in phytoplankton and display a wide range of values, likely depending upon sample composition and the presence of Ba-Ra seeker species in plankton mixed samples. These concentrations are about double those in macroalgae, and lower concentrations were determined in other taxa such as zooplankton, crustacean, fish and molluscs. In the same groups, the average values for ^{228}Ra are also at the same level as ^{226}Ra, although likely to vary more depending upon sample origin.

This summary also shows that ^{228}Ra concentrations tend to be slightly higher than those of ^{226}Ra in the same samples (Table 3.27, based on Ref. [3.202]). This trend of slightly higher ^{228}Ra concentrations was also present in a compilation of data made by Iyengar and Rao [3.203]. However, higher ^{228}Ra is reported systematically for calcified structures, namely mollusc shells, crustacean exoskeleton and fish bone, suggesting that the ^{228}Ra in such structures may be due to uptake of ^{232}Th, and ^{228}Ra ingrowth after deposition. In biota soft tissues, such as fish fillet and mussel soft tissues, the concentration ranges of ^{226}Ra and ^{228}Ra are similar [3.203]. For both radionuclides, activity concentrations were always higher in calcified structures than in soft tissues, indicating general accumulation of Ra in tissues with high calcium content.

TABLE 3.27. AVERAGE ACTIVITIES OF ^{226}Ra AND ^{228}Ra IN MARINE ORGANISMS MAINLY FROM THE GULF OF MEXICO

Taxon	Concentration range (Bq/kg DW)		Arithmetic mean	SD	Geometric mean
	Min	Max			
^{226}Ra					
Phytoplankton	1.04	333.0	74.00	117.66	16.28
Macroalgae	0.11	44.40	16.65	13.32	9.25
Seagrass	2.52	7.40	4.81	—	—
Zooplankton	0.41	90.28	24.42	33.30	4.81
Crustaceans	1.48	48.10	10.73	15.54	5.18

TABLE 3.27. AVERAGE ACTIVITIES OF ^{226}Ra AND ^{228}Ra IN MARINE ORGANISMS MAINLY FROM THE GULF OF MEXICO (cont.)

Taxon	Concentration range (Bq/kg DW)		Arithmetic mean	SD	Geometric mean
	Min	Max			
Molluscs	0.41	13.32	4.07	4.07	2.29
Fish (whole body)	0.11	13.32	2.81	4.07	1.55
Fish (bone)	0.26	25.90	5.92	7.40	3.07
^{228}Ra					
Phytoplankton	18.5	92.5	55.5	—	—
Macroalgae	4.44	129.8	28.49	26.64	19.24
Seagrass	7.4	49.95	28.86	—	—
Zooplankton	1.813	67.34	26.64	26.64	11.1
Crustaceans	0.592	129.8	28.49	44.77	6.66
Molluscs	1.739	70.3	17.39	23.31	7.4
Fish	1.332	99.9	31.08	35.15	9.99
Fish (bone)	2.331	166.5	47.36	60.68	19.61

Both the data sets mentioned above [3.202, 3.203], although given on both a dry weight and a wet weight basis, are useful to inspect trends across the taxa of marine biota. Excluding bone tissue and calcified structures in general, higher Ra concentrations were measured in phytoplankton and macrophytes, while concentrations in the soft tissues of molluscs, crustaceans, fish and mammals were consistently low and often below 2 Bq/kg (WW) (Tables 3.27 [3.202] and 3.28 [3.200]). Clearly, it seems that Ra transfer through the food chain is very low. Probably the best illustration for this non-transfer of Ra with diet is sardines, which are specialist plankton feeders mostly feeding upon phytoplankton and possibly some zooplankton. In spite of the relatively high ^{226}Ra concentrations in plankton, sardines do not display ^{226}Ra concentrations higher than tuna do, or even higher than a large marine mammal such as the sperm whale feeding upon large cephalopods (Table 3.28).

TABLE 3.28. CONCENTRATIONS OF NATURALLY OCCURRING RADIONUCLIDES (mBq/KG WET WEIGHT ± 1SD) IN THE MUSCLE TISSUE OF MARINE SPECIES

Species	DW/WW	^{238}U	^{234}U	^{226}Ra	^{210}Pb	^{210}Po
Sardine *Sardina pilchardus*	0.23	24 ± 2	25 ± 2	4×10^2	1×10^3	3×10^4
Tuna *Thunnus alalunga*	0.27	2.8 ± 0.2	2.8 ± 0.2	6×10^2	5×10^2	5×10^3
Blue marlin *Makaira nigricans*	0.35	8.5 ± 0.9	9.6 ± 0.9	5×10^2	—	4×10^2
Sperm whale *Physeter catodon*	0.27	2.9 ± 0.3	2.9 ± 0.3	5×10^2	4.5×10^2	5×10^3

Note: Relative SD, where not indicated, is approximately 10% or less.

Radium activity concentration in muscle of a range of commercial fish species from the North Atlantic, including plaice, halibut, cod and round nose grenadier, and occupying different ecological niches, ranged from 0.156 to 0.876 Bq/kg (WW), which underscores the insignificant role of food chain transfer in ^{226}Ra accumulation in marine fish [3.204].

Radium-226 activity concentration in marine biota was compared with the activity concentrations of other naturally occurring and artificial radionuclides in fish muscle (Table 3.29 [3.204])). In several marine species, ^{226}Ra concentrations fluctuate within a narrower range than other radionuclides, such as ^{210}Po. In all species, analysed ^{226}Ra activity concentrations were lower than those of ^{40}K, ^{210}Pb and ^{210}Po, the latter clearly transferred by ingestion and enhanced in marine food chains, with little direct uptake from seawater [3.201, 3.204].

3.11. RADIUM IN DRINKING WATER AND FOOD

Food and water ingestion are the primary sources for radionuclide transfer to humans. Therefore, Ra isotope concentrations in various foodstuffs and drinking waters were always a subject of much research.

Radium in drinking water arises from various natural and artificial sources, mainly due to the interaction of ground or surface water with Ra bearing materials such as rocks, soil, ore bodies, etc. The concentrations of Ra in drinking water depend on the source by which it comes to the water, including the amount of Ra in the source, processes that release the Ra away from the matrix and the efficiency of operation of water cleaning mechanisms. In addition, Ra isotopes occur as members of decay series, thus, there will be a compound effect of similar processes along the various decay series if the source of the Ra contains precursor radionuclides such as natural U and Th [3.205]. Countrywide data on Ra isotopes in drinking water according to the UNSCEAR [3.6] are presented in Table 3.30.

The data in Table 3.30 show that Ra concentrations in drinking water vary across a wide range from the detection limit to 49 000 mBq/L. High levels of ^{226}Ra and ^{228}Ra have been found to be associated with areas surrounding U or Th ore bodies [3.3]. Rather low mean concentrations of Ra isotopes have been observed in the public water supply system where the water passes through cleaning systems. Therefore, a value of 0.5 mBq/L was assumed by the UNSCEAR [3.6] for worldwide assessments.

Extremely high levels of ^{226}Ra in drinking water have been found in Finland. According to the authors of the study [3.24], this is due to elevated U or ^{226}Ra levels in the area’s bedrock. Thus, the groundwater of the Helsinki region is considered to be anomalous in character with respect to its natural radiation.

Bottled mineral water is widely consumed in many countries and the Ra concentration in such water is of high interest. Philippe [3.25] has investigated some of this water in Bulgaria, France, Greece, Lebanon, Saudi Arabia and the United Arab Emirates, along with water of local origin. He found that ^{226}Ra concentrations in mineral water ranged from 163 to 392 mBq/L, which agrees well with the reported values of 55.5 to 500 mBq/L for local and imported bottled water sold in the USA [3.206].

Data on ^{226}Ra in different foodstuffs, adapted from the UNSCEAR [3.5] review, are given in Table 3.31.

TABLE 3.29. CONCENTRATION OF RADIONUCLIDES IN FISH MUSCLE (WW) OF COMMERCIAL SPECIES FROM NORTH ATLANTIC

Species	DW/ WW	^{238}U (mBq/kg)	^{235}U (mBq/kg)	^{234}U (mBq/kg)	^{226}Ra (mBq/kg)	^{210}Pb (mBq/kg)	^{210}Po (mBq/kg)	^{137}Cs (mBq/kg)	^{40}K (mBq/kg)
Cod *(Gadus morhua)*	0.19	2.0 ± 0.3	0.12 ± 0.12	2.6 ± 0.4	24.4 ± 2.5	49.6 ± 2.4	23.0 ± 1.6	0.18 ± 0.03	140 ± 4
Cod *(Gadus morhua)*	0.18	2.8 ± 0.9	0.6 ± 0.6	3.6 ± 0.9	15.6 ± 1.6	24.9 ± 2.0	64.7 ± 4.4	0.26 ± 0.03	138 ± 4
Cod *(Gadus morhua)*	0.19	6.0 ± 0.9	0.4 ± 0.4	5.8 ± 0.9	19.2 ± 1.5	17.1 ± 2.0	487 ± 18	0.17 ± 0.03	122 ± 3
Greenland halibut (*R. hippoglossoides*)	0.19	3.5 ± 04	0.13 ± 0.13	4.6 ± 0.5	26.3 ± 1.9	50.3 ± 2.1	130.8 ± 9.1	0.15 ± 0.03	101 ± 3
Plaice (*H. platessoides)*	0.24	3.5 ± 0.7	0.13 ± 0.13	8.1 ± 0.1	34.9 ± 3.1	—	182.3 ± 8.7	0.21 ± 0.03	119 ± 3
Greenland halibut *(R.hippoglossoides)*	0.30	12.7 ± 0.5	0.52 ± 0.08	16.4 ± 0.6	103 ± 9	12 ± 2.0	410 ± 57	—	—
Redfish *(Sebastes mentella)*	0.22	8.1 ± 0.3	0.17 ± 0.03	8.5 ± 0.3	510 ± 66	204 ± 19	478 ± 24	0.21 ± 0.05	152 ± 4
Ray *(Raja centa)*	0.20	6.1 ± 0.2	0.54 ± 0.08	3.4 ± 0.1	89 ± 1.3	138 ± 10	5522 ± 262	—	—
Round nose grenadier (*C. rupestris)*	0.15	24.1 ± 1.0	1.6 ± 0.2	30.9 ± 1.2	324 ± 36	136 ± 9.0	233 ± 11	0.10 ± 0.03	95 ± 3
Red hake (*Urophycis chuss)*	0.07	210 ± 9.0	7.8 ± 1.4	193 ± 9.0	702 ± 74	65 ± 5.0	4489 ± 218	n.d.	32 ± 1
Kitefin shark (Dalatias licha)	0.10	26.1 ± 1.2	0.87 ± 0.18	34.6 ± 1.6	387 ± 47	14 ± 1.0	29 ± 3.0		
Redfish *(Sebastes mentella)*	0.20	12.0 ± 0.5	0.10 ± 0.01	9.0 ± 0.4	445 ± 50	200 ± 20	480 ± 20	n.d.	116 ± 4

— = no data available
n.d. = not detectable

TABLE 3.30. ACTIVITY CONCENTRATIONS OF RADIUM ISOTOPES IN DRINKING WATER (mBq/L)

Country	Origin	^{226}Ra		^{228}Ra	
		Mean	Range	Mean	Range
United States of America	Drinking water		0.4–180		0–0.5
Argentina	Private wells	2.24	<0.3–22		
	Bottled water	1.3	<0.3–2.4		
Brazil	Mineral water	27	8.0–83	97	12–385
Finland	Drinking water		10–49000		18–570
France	Drinking water		7–700		
Germany	Drinking water	5	0.5–32	3	0.5–23
Italy	Tap water		<1.2–23		1.5–12
	Mineral water		0.5–126		0.1–44
Portugal	Drinking water	27	<3–2 185		
Spain	Public supply	1.75	1.3–2.2	<84.5	
	Bottled water	86.7	2–600		
Switzerland	Drinking water		0–200		5–300
United Kingdom	Drinking water		0–180		
Czech Republic	Public supply	28	40–302		
Hungary	Public supply	43	8–238		
Poland	Drinking water		1.7–4.5		
Romania	Drinking water		0.7–21		
Russian Federation	Water supply	7.4	2.6–23.4	12.6	2.4–34

TABLE 3.31. MEAN CONCENTRATIONS OF ^{226}Ra IN FOODS

Products	Region	Country	^{226}Ra, Bq/kg
Milk products	North America	United States	5.7
	Asia	China	6
		Japan	12
	Europe	Italy	3–19
		Germany	2–130
		Poland	10
		Romania	0.9–44
		United Kingdom	0.4–200
Meat products	North America	United States	20
	Asia	China	41
		Japan	46
	Europe	Germany	30–220
		Poland	11–19
		Romania	2–30
		United Kingdom	2.6–74
Grain products	North America	United States	7–100
	Asia	China	17
		Japan	14
	Europe	Germany	20–2900
		Poland	80–110
		Romania	30–90
		United Kingdom	0.7–5200
Leafy vegetables	North America	United States	56
	Asia	China	75
	Europe	Italy	27–44
		Germany	6–1150
		Poland	37–43
		United Kingdom	2.2–170

TABLE 3.31. MEAN CONCENTRATIONS OF ^{226}Ra IN FOODS (cont.)

Products	Region	Country	^{226}Ra, Bq/kg
Root vegetables / fruits	North America	United States	7 –47
	Asia	China	63
		Japan	11
	Europe	Italy	14–25
		Germany	5–9400
		Poland	11–215
		Romania	9–190
		United Kingdom	9.0–41
Fish products	North America	United States	30–59
	Asia	China	39
	Europe	France	37
		Germany	100–7400
		Poland	28–43
		United Kingdom	8.5–2100

Concentrations of naturally occurring radionuclides in foods vary widely around the world (and even within a given country) because of the differing Ra concentrations in the rocks, soils or ore bodies and therefore in the water and air.

Concentrations of ^{226}Ra in animal products are slightly lower than those in plant products. The concentrations of ^{226}Ra in milk and meat vary from 0.4 to 200 Bq/kg and from 30 to 220 Bq/kg, respectively. These ranges are much wider for plant products, 0.7–5200 Bq/kg, 5–9400 Bq/kg and 2.2–1150 Bq/kg for grain, root and leaf vegetables, respectively. Although the upper range for the fish products (7,400 Bq/kg) is slightly lower compared to root vegetables, the highest mean ^{226}Ra concentrations were found to be in fish products.

Based on these data, the UNSCEAR adopted the following values as reference concentrations for worldwide dose assessments: 5 Bq/kg in milk, 15 Bq/kg in meat, 80 Bq/kg in grain, 50 Bq/kg in leafy vegetables, 30 Bq/kg in root vegetables and 100 Bq/kg in fish. However, there are a number of circumstances in which the concentrations of natural radionuclides in ingested food and water substantially exceed the reference concentrations or the more typical range of variation. In particular, elevated Ra concentrations in soils in some agricultural regions of Germany, Poland or the UK may result in higher concentrations of this radionuclide in many foodstuffs. However, since not all components of the diet are affected, and because of widespread distributions of foods of many different origins over larger regions, the doses to individuals in local populations in such locations are not usually substantially elevated [3.5].

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Chapter 4

ENVIRONMENTAL PATHWAYS AND CORRESPONDING MODELS

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4.1. CONCEPTS

Radionuclides released to the environment are distributed throughout the different environmental media (air, water, soil and sediment) through various physical and chemical processes. Some of the radionuclides in the environmental media are taken up by the organisms which live in the respective environments and by people who use the environment or consume foods from the environment. Humans and other organisms are also exposed to external gamma radiation from radionuclides in the environmental media. The ways in which humans and other organisms are exposed to radiation and radiation in the environment are described in the following sections.

4.1.1. General approach

Figures 4.1 and 4.2 provide a general illustration of the various ways in which humans and other organisms can be exposed to radiation and radionuclides in the environment. Figure 4.1 illustrates how radionuclides are transferred through the environment and interact with organisms. Figure 4.2 provides a simplified representation of how humans who live in, or otherwise use, a particular environment are exposed to radiation and radionuclides.

In brief, Fig. 4.1 illustrates the transfer between environmental media and organisms as well as interactions between the organisms. This is shown, for example, by radionuclides present in the air and in rain being transferred into the aquatic environment. The aquatic environment has different components. In the case of the freshwater environment, this includes streams, rivers, lakes and sediments, while the marine environment includes tidal zones, coastal waters and marine sediments. Radionuclides can then be transferred into a wide range of of organisms such as plants, phytoplankton, zooplankton, macroinvertebrates, sessile aquatic plants, fish, water based amphibians, crustaceans, mammals and birds that obtain dietary components from the aquatic (freshwater/marine) environment.

Radionuclides can also be transferred into the terrestrial environment, for which the most important media is soil. They can then be taken up into terrestrial organisms such as plants, invertebrates and vertebrates (mammals, birds, reptiles and land based amphibians).

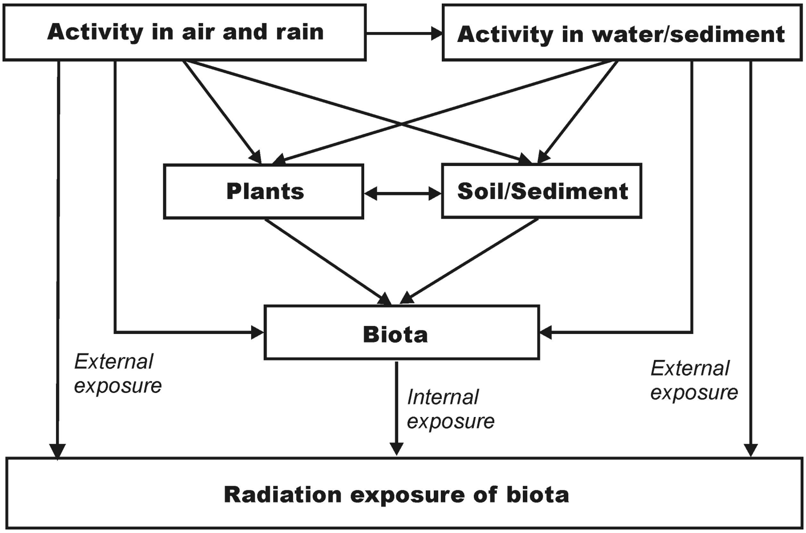

FIG. 4.1. Example of general radiation exposure pathways to biota (adapted from Ref. [4.1]).

Terrestrial and aquatic environments are not totally separate since some terrestrial organisms obtain food or drinking water from the aquatic environment. For example, bears eat fish, and moose and waterfowl feed on aquatic plants. Therefore, care is needed in defining in the conceptual model the ways in which such animals may be exposed.

The simplified representation provided in Fig. 4.2 illustrates the ways in which people are exposed to radiation in the various environmental media with which they interact. For example, people take radionuclides into their bodies via the air they breathe, the water they drink and the food they eat. Intake via foodstuffs consumed by people (‘diet’) will depend greatly on individual habits and diets. For example, many people will consume only food they purchase from local grocery stores while others may rely on food they grow, hunt or catch.

The approaches, models and parameters used to describe environmental behaviour in the terrestrial and aquatic ecosystems are described below in Sections 4.1.2 to 4.1.5.

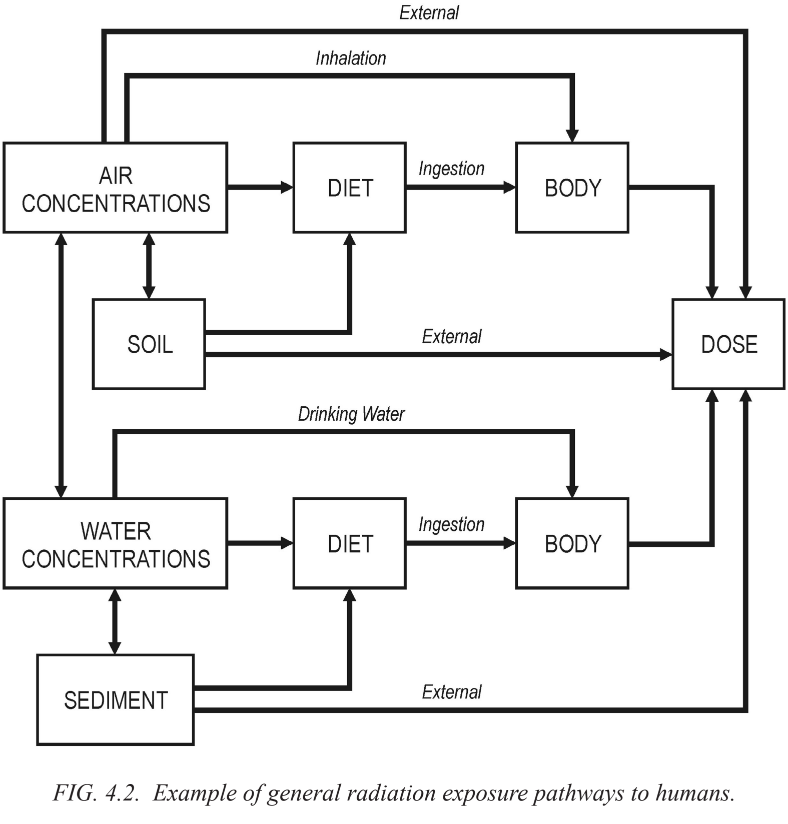

FIG. 4.2. Example of general radiation exposure pathways to humans.

4.1.2. Reference plants and animals

There is a vast array of biota that can be considered in the development of a conceptual model. However, it is not possible to aquire information for all biota. Therefore, the concept of a set of reference organisms that are representative of common ecosystems has been developed by the International Commission on Radiological Protection (ICRP) [4.2] to focus the effort on methods and data needed. This approach provides a strategy that allows assessment efforts to be focused and thereby reduced to a more manageable size. The twelve reference animals and plants (RAPs) selected by the ICRP cover a range of global ecosystems and taxonomic families. In an analysis of a specific site, the analyst is able to augment the ICRP's reference animals and plants with plants or animals with characteristics more relevant to the local setting, for example caribou in northern Canada or Scandinavia.

The first step in an ecological risk assessment involves developing a conceptual model of the study area including the media and biological environments, the sources of radiation and the pathways and routes of exposure for relevant representative organisms. The main criteria for the selection of reference organisms include the habitats and feeding habits of an organism that maximize potential exposure to radionuclides and the potential accumulation of radionuclides by an organism, and thus are likely to maximize internal exposures.

4.1.3. Reference dose levels

Data on effects to non-human biota arise from various experimental designs both in the laboratory and in the field, from results of studies on environments that have been exposed to elevated levels of radiation resulting from normal operations of nuclear facilities and waste management activities, as well as from studies of areas impacted by accidents. These data have recently been reviewed [4.1]. Based on its review of available data and considering the overall limitations of the data, the UNSCEAR concluded that data developed since its 1996 report [4.3] did not support changes to its previous recommendations for reference dose rates below which population level effects on non-human species are unlikely. Hence, the UNSCEAR concluded that chronic dose rates of less than 100 μGy/h to the most highly exposed individuals would be unlikely to have significant effects on most terrestrial communities and that maximum dose rates of 400 μGy/h to any individual in aquatic populations of organisms would be unlikely to have any detrimental effect at the population level. Similar conclusions were made also in the ICRP report [4.2].

To interpret the results of these studies, it is important to have a clear understanding of the relationship between the levels of radiation and activity concentrations of radionuclides in the various environmental media in which the organism resides, the consequent dose rate to an organism (or a tissue or organ of the organism) that lives in the environment and the biological effect of interest. For example, for a given distribution of radionuclides in the ambient environment, biota can be directly irradiated externally or internally as a result of radionuclides being taken into the organism via inhalation, ingestion, or uptake through skin or membrane. Empirically determined concentration ratios are commonly used to estimate contaminant concentrations in the organism (e.g. expressed for wet or dry weight in units of Bq/kg) from concentrations in the ambient environment (e.g. expressed in units of Bq/kg for sediment or soil and 1 Bq/L for water) [4.4].

4.1.4. Dosimetric models

Dosimetric models are used to convert exposures to doses. Dose coefficients are available for selected non-human biota; they relate ambient concentrations to internal and external exposure and hence to dose. Similarly, dose coefficients are available for estimating the dose to humans from radionuclides taken into the body. Dose coefficients for non-human biota and for humans are discussed in Chapter 5.

4.1.5. Model complexity

In broad terms, three general classes of radioecological models of increasing complexity can be distinguished: equilibrium models, dynamic models and research models.

Equilibrium models, such as those used by UNSCEAR [4.1], are primarily intended for the assessment of exposures due to routine releases into air and water. They assume that the release rates of the radionuclides are approximately constant in time and that the duration of the releases is sufficient for radionuclide concentrations to reach (near) equilibrium within each of the environmental compartments. In this situation, the transfers between compartments are easily characterized by time invariant ratios of concentrations between acceptor and donor compartments. This type of equilibrium radioecological model is widely used except in situations with rapidly changing releases, for example, following accidents. For this type of scenario, a dynamic model that can make estimates of dose under changing radionuclide concentrations can be employed. Equilibrium models are assumed in this report unless specifically noted otherwise.

4.2. TERRESTRIAL ENVIRONMENT

4.2.1. Soil–radium interactions

4.2.1.1. Radium chemistry in soil

Radium is the heaviest of the Group II alkaline earth metals. Like Ba, Sr and Ca, which also belong to Group II, Ra forms insoluble sulphate, carbonate and chromate salts. The chloride, bromide, nitrate and hydroxide salts of Ra are soluble in water. In general, Ra salts are less soluble than are corresponding Ba salts [4.5]. Discrete Ra minerals such as $RaSO_4$ are not reported in earth materials and the Ra concentrations in water in contact with soil or sediments are reduced by sorption (e.g. by hydrous oxides of Fe, Al and Mn) and co-precipitation reactions [4.6].

Adsorption and ion exchange processes are particularly important in determining the rate of Ra transport in any groundwater/soil system. Cation exchange equilibrium is dominated by (a) coulombic interactions between cations (in various states of hydration) and the fixed groups of the exchanger material; and (b) ionic hydration effects caused by ion-dipole interactions with water molecules [4.7]. When ionic hydration effects predominate, ions of smaller hydrated radius tend to displace ions of larger hydrated radius, and the affinity series for adsorption (or ion exchange) follows the order:

$$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$$

since Ra^{+2} forms the smallest hydrated ion [4.8].

If coulombic interactions between cations and the exchange site predominate, then the selectivity is reversed [4.7].

Ra^{2+} is moderately soluble in natural water, although a high sulphate (SO_4^{2-}) content will favour its removal as mixed sulphate crystals, such as $Ba(Ra)SO_4$, or, for high CO_2 water, removal as $(M,Ra)CO_3$. High sulphate concentrations may provide for the formation of $RaSO_4$, although Ra^{2+} concentrations rarely approach the solubility limit. Radium in solution is not strongly dependent on anionic species and forms sulphate, but not carbonate, complexes [4.9].

The environmental distribution of Ra varies depending on its origin. Nevertheless, according to Dyck and Jonasson [4.10], the processes affecting distribution can be analysed by referring to the following main (simplified) equations:

$$Ra^{2+} + Ba^{2+} + Ca - (clay) \rightarrow Ca^{2+} + Ra - (clay) - Ba \quad \text{adsorption}$$
$$xCa^{2+} + (l-x)Ra^{2+} + MCO_3 \rightarrow Ca_xRa_{1-x}CO_3 + M^{2+} \quad \text{co-precipitation}$$

$Ra^{2+} + SO_4^{2-} \rightarrow RaSO_4$ surface reaction
$Ra^{2+} + 2Cl^- \rightarrow RaCl_2$, etc.... soluble species

The scavenging effects of clays, organic debris and hydrous oxides outweigh the dissolution of Ra by chloride in the surficial environment and result in a net deficit of Ra in stream water entering the oceans.

4.2.1.2. Radium sorption: the solid–liquid distribution coefficient (K_d)

Dissolved radionuclide ions can bind to solid surfaces by a number of processes often classified under the broad term of sorption. Sorption is element and soil type dependent, and is affected by soil mineralogy (e.g. clay content and type, iron oxides and hydroxides), by organic matter content and soil geochemistry (pH, presence of colloids, presence of counter-ions, etc.) and by the experimental method used for its quantification.

The behaviour of radionuclides in soils is largely controlled by their chemical form and speciation, which strongly affect their mobility, their residence time within the soil rooting zone and uptake by biota. The ionic strength of the surrounding fluid exerts a primary control on the Ra K_d; contact with groundwater containing dissolved salts reduces the K_d significantly (see Section 2.4.4).

The K_d is based on the equilibrium concept. It relies on the hypothesis that the radionuclide on the solid phase is in equilibrium with the radionuclide in solution, and can thus exchange with it. However, elapsed time since the addition of the radionuclide affects the value of K_d, since a fraction of the added radionuclide may become fixed by the solid phase (an aging effect related to sorption dynamics). Most laboratory tests are, in principle, designed to obtain the so-called exchangeable K_d (K_d^{exch}). However, a K_d deduced from a laboratory test cannot be unequivocally considered to be a K_d^{exch}, since the nature of the sorption process for a given radionuclide may lead to a quasi-instantaneous irreversible sorption (or co-precipitation on soil components). In other cases such as long contact times, a fraction of the radionuclide present may become irreversibly sorbed, and thus no longer participates in the soil–soil solution equilibria [4.11]. For many experimental data, only a pseudo equilibrium may be reached as sorption processes associated with the absorption on clay lattices can be slow and equilibrium may not be reached during the time available for the experiments. Hence, the large number of approaches used to quantify K_d values, and the contrasting experimental conditions applied in each case, lead to wide ranges of K_d values being obtained [4.4, 4.12].

For field experiments, K_d values can be quantified from the radionuclide concentration in the solid phase divided by the concentration of the radionuclide in the soil solution obtained from the contaminated soil. This approach may lead to higher K_d values than those resulting from a laboratory sorption test, because the radionuclide quantified in the solid phase of the contaminated soil may include sorbed radionuclide not available for exchange with the soil solution if there has been a sufficiently long period of time for this process to take place.

4.2.1.3. Effect of soil properties on radium sorption

Johnston and Gillham [4.13] state that Ra is present as Ra^{2+} over the pH range 4–8 and does not readily form complex species. Radium could be expected to co-precipitate with $BaSO_4$, carbonates and ferric hydroxides, and the presence of these compounds in the soil may lead to overestimated Ra K_d values. Since Ra generally occurs in nature as a divalent cation, it therefore has a high affinity for the regular exchange sites of the soil.

Johnston and Gillham [4.13] have correlated K_d values with soil CEC. Arnold and Crouse [4.14] obtained a correlation between Ra adsorption and the CEC. The leaching studies reported by Havlik et al. [4.15] support the view that cation exchange is an important mechanism for Ra adsorption. Nathwani and Phillips [4.16] showed that organic matter and clay play a significant role in the adsorption of ^{226}Ra, with organic matter adsorbing approximately ten times as much Ra as clays. The retaining power of organic matter and clays for ^{226}Ra was predominantly due to the CEC. Vandenhove and Van Hees [4.17], exploring the effect of soil properties on Ra availability in a small scale study covering 8 soils, concluded that K_d (Ra) could be predicted by CEC [K_d (Ra) = 0.71 × CEC – 0.64, R^2=0.91] and soil organic matter content [K_d (Ra) = 27 x OM − 27, R^2=0.83]. Haji-Djafari et al. [4.18] found sorption of Ra to increase with soil pH (K_d= 12 L/kg and 100 L/kg at pH 4.5 and 7, respectively) and Russanova [4.19] monitored desorption decreases with pH (5–10 times higher desorption at pH 3 than at pH 6–10;). Calcium concentrations in the soil solution or exchangeable phase significantly affect K_d (Ra) values. (Nathwani and Philips [4.16] reported that K_d (Ra) decreased more than tenfold when external Ca^{2+} concentrations changed from 0.005 to 0.05 M) (Fig 4.3).

4.2.1.4. Radium speciation in soil

The speciation of heavy metal ions in the soil is frequently studied using sequential extraction procedures [4.20] which can indicate the proportion of the metal bound to different soil components (such as the readily exchangeable fraction, the fraction bound to carbonates, to iron and manganese oxides, to organic matter and to residual ions). However, the sequential extraction technique, as described by Tessier et al. [4.20] and others, has several shortcomings, notably that a particular extraction is never complete and may not fully distinguish the

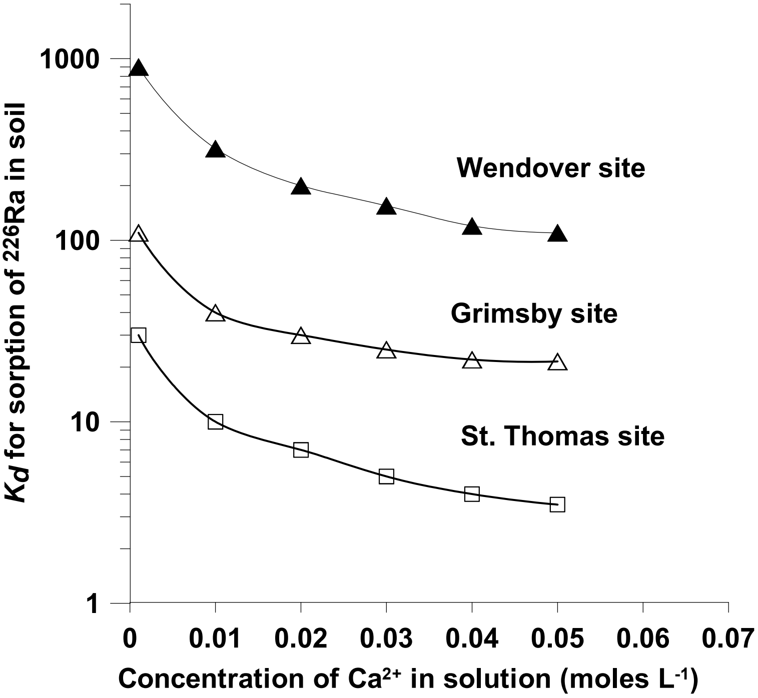

FIG. 4.3. K_d for sorption of ^{226}Ra by soils as a function of Ca^{2+} concentration in solution (adapted from Nathwani and Phillips [4.16]).

different speciation forms. Additionally, many practical difficulties exist, some of which have been described by Benes et al. [4.21]. Despite these reservations, various data on Ra extractions have been reported, some of which are decribed below.

Lima and Penna-Franca [4.22] observed that in farm soils from a highly radioactive region in Brazil, approximately 50% of ^{226}Ra was associated with the residual fraction, 30% with oxides of Fe and Mn, 15% was organically bound, 5% was associated with carbonates and only 3% was in an easily exchangeable form. Similarly, Bunzl et al. [4.23] found that for a soil close to the exhaust of the ventilating shaft of a U mine, 6% of the ^{226}Ra was associated with the exchangeable fraction, 15% each was associated with the organic and oxide fraction and 66% was in the residual fraction. For soils outside the area of impact, no ^{226}Ra was found in the exchangeable and organic fractions, 3% was associated with the oxide fraction and more than 90% was in the residual fraction. In contrast, for two Australian soils, Cooper et al. [4.24] found that the majority of Ra was associated with the exchangeable fraction and with iron and manganese oxides.

Dowdall and O'Dea [4.25] applied a sequential extraction technique according to Greeman and Rose [4.26]. For upland organic soils overlaying a uraniferous granite, 2% of ^{226}Ra and 12% of ^{228}Ra was in the exchangeable fraction, respectively; 3% and 9% was associated with easily oxidisable organic matter and 9% and 20% was associated with iron oxides. The discrepancy in ^{226}Ra and ^{228}Ra behaviour was attributed to the different behaviour of the respective parent radionuclides. Averaging of the total labile radionuclide content (exchangeable, associated with easily oxidizable organic matter and with Fe oxides) yielded values of 12% for ^{226}Ra, 41% for ^{228}Ra and 81% for ^{238}U. These figures appear to confirm the generally accepted hypothesis that Ra is relatively less mobile than U [4.25, 4.27].

4.2.1.5. Radium K_d values

Sheppard et al. [4.28] recommended a K_d (Ra) value of 47 L/kg (n=37) irrespective of soil type since the K_d values per soil class were not significantly different, and also proposed a downward revision of the earlier TRS 364 estimates (IAEA [4.29]; extracted from Sheppard and Thibault [4.30]), where values of 490, 36, 000, 9000 and 2400 L/kg were recommended for sand, loam, clay and organic groups, respectively.

The IAEA [4.4, 4.12] and Vandenhove et al. [4.31] presented K_d values for Ra classified according to the texture and organic matter criteria. These values are applicable to water with low ionic strength (Table 4.1, [4.12]). Geometric means were highest for clay soils and lowest for loam soils. Considering the high affinity of Ra for the regular exchange sites [4.32], the higher K_d (Ra) value observed for clay soils than for loam soils can be explained by the generally higher CEC of clay soils, which thus have a higher sorption capacity.

K_d (Ra) estimates were generally not significantly different between soil groups, with values varying by 2 to 5 orders of magnitude. For clay soils, and especially for organic soils, very low numbers of K_d measurements were available which made it difficult to deduce best estimates for these groups. The overall geometric mean proposed in a more recent IAEA [4.4, 4.12] compilation (2500 L/kg) is 2 orders of magnitude higher than that of Sheppard et al. [4.28].

Though the classification of K_d values by soil group did not result in significant differences between the soil classes, a more suitable parameter for classifying K_d values (e.g. pH, CEC, OM) has not been suggested either [4.12, 4.31]. Additional research to collate K_d (Ra) values, especially for clayey and organic soils is recommended. Furthermore, a more methodical soil characterization is advised to be able to deduce the processes determining Ra sorption and to allow for prediction of K_d (Ra) from soil parameters.

TABLE 4.1. K_D (Ra) (L/KG) FOR SOILS GROUPED ACCORDING TO THE TEXTURE/OM CRITERION FOR WATER OF LOW IONIC STRENGTH

Soil group	K_d				
	n	Geometric mean	Geometric SD	Minimum values	Maximum values
All soils	51	2.5 x 10^3	13	12	950 000
Sand	20	3100	8	49	40 000
Loam	19	1100	17	12	120 000
Clay	6	38 000	12	696	950 000
Organic	1	—	—	—	—
Unspecified	4	1200	1	785	1890

— = no data available

4.2.1.6. Vertical mobility of radium in undisturbed soil profiles

The relation between the migration rate of Ra, V_{Ra} (cm/s), and the migration rate of the liquid phase (cm/s) is given by:

$$V_{\mathrm{Ra}} = V_{\mathrm{H_2O}} \left(\frac{1}{1+\rho \frac{K_d}{\theta}} \right) \tag{4.1}$$

With a precipitation surplus (precipitation − evapotranspiration) of 20 cm per year, a bulk soil density ρ of 1.4 g/mL and a moisture content θ of 0.2 mL/mL and assuming an average soil K_d value of 2500 L/kg, the interstitial is 100 cm/a, while V_{Ra} is about 0.005 cm/a. This is a low average migration rate which will be exceeded by bioturbation processes, by the formation or disappearance rates of the soil itself due to erosion and by aeolian deposition [4.33].

Migration theory also includes exchange equations, and sorption and desorption of Ra are controlled by exchange reactions. Hence, the basic processes controlling mobility of radionuclides (and other trace elements) in soil include convective transport by flowing water, dispersion caused by spatial variations of convection velocities, diffusive movement within the fluid and physicochemical interactions with the soil matrix.

The two most common approaches for modelling the migration of radionuclides in soils are (a) a serial compartmental approach where vertical migration in soil is expressed as migration rates (cm/a), mostly based on the previously described K_d concept approach; and (b) a convection–dispersion approach described by a convection velocity (cm/a) and an effective (or apparent) dispersion coefficient (D: cm^2/a). A description of both modelling approaches is presented by Strebl et al. [4.34]. Owing to the high degree of adsorption, diffusion processes do not influence the long distance transport mechanism of Ra. In general, equilibrium exists in soil between Ra in solution, Ra adsorbed onto exchangeable sites of the soil surface and Ra incorporated within soil particles.

Diffusion is, however, important for processes which can be described as 'stripped leaching'. When exchangeable Ra is stripped off by leaching, as occurs frequently in uranium mine tailings [4.33], the incorporated Ra will diffuse to the surface until the equilibrium is again established. When stripped leaching is continuously applied, the leaching rate is diffusion controlled.

Some experimental studies have highlighted the limited mobility of Ra within soil. For example, in studies where Austrian soils in cropped and ploughed lysimeters were artificially contaminated (spiked) with soluble Ra and then monitored for nine years, low migration velocities (0.4 cm/a or less) were observed [4.35].

Kribek [4.36] reported that the vertical distribution of Ra in soil profiles in an area of U mining depended on the type of soil profile. In flood plain soil significantly contaminated by Ra owing to periodic flooding with river water receiving mine effluents, approximately 79% of the Ra contained in the top 60 cm of the soil was accumulated in the 0–10 cm layer and 18% in the 10–25 cm layer. The limited Ra migration was much higher than would be expected from K_d based models, and particle mediated transport probably played an important role.

Wetland soils (14–50% organic matter) in Ireland showed $^{226}Ra/^{238}U$ activity ratios of up to 9.0. Assuming initial isotopic equilibrium in soil (i.e. $^{226}Ra/^{238}U = 1.0$), the elevated ratios suggest a loss of ^{238}U relative to ^{226}Ra. The largest ratios were seen in depth zones that are only saturated at certain times of the year. This result reflects the relative immobility of Ra with respect to U under oxidizing conditions [4.27].

Leaching of Ra from Port Hope soils was significantly affected by texture and organic matter: leached amounts were much greater for soils with coarser and intermediate size fractions and low organic matter content ($D = 10^{-4} - 10^{-7}$ cm^2/a) than for fine textured soils with higher organic matter content ($D = 10^{-7} - 10^{-10}$ cm^2/a) [4.16].

Because an acid environment increases leachability, solubility, and thus mobility, increased leaching would be expected in tailings from the sulphuric acid process in mines. However, during repeated extractions of soil from vegetated tailings using distilled water, the pH values of consecutive extractions increased from 4 to 6 and only 0.24% of the ^{226}Ra was leached (Ibrahim et al. [4.37]). As Ra sulphate is a highly insoluble compound, very limited migration would be expected even in acidic circumstances.

In addition to abiotic processes, soil micro and macrofauna may contribute to the transport of radionuclides in the soil surface layers. Earthworms may bring down decomposing organic matter to a depth of approximately 1 m, and it is possible that the pathway of uptake of Ra by vegetation and subsequent downward transport of plant litter through action of earthworms exceeds the physicochemical migration in some soils. The production of complexing agents by microorganisms may also enhance Ra solubility and leaching but it is currently difficult to provide a quantitative description of the process [4.33].

4.2.1.7. Soil losses following washoff

Radionuclide transport with water from contaminated watersheds is an intermittent flux — also called watershed washoff (or catchment runoff) — which causes radionuclide redistribution in terrestrial ecosystems, and, more critically, radionuclide inputs into downstream water bodies. Mean washoff fluxes and their evolution with time can be generally quantified via two types of parameters: liquid and solid entrainment coefficients and transfer functions [4.38, 4.39]. Garcia-Sanchez [4.38] provides an extensive review of transfer by washoff from watersheds covering various radionuclides, source terms, processes, time and space scales reported in the literature after 1960. No data are available related to Ra, but data for ^{90}Sr could give an indication of anticipated washoff for Ra. The fraction of deposited ^{90}Sr removed via short term washoff varied between 0.1 and 7.2%.

4.2.2. Radium soil to plant transfer

4.2.2.1. The concept of the radium soil to plant concentration ratio

There are several parameters that are commonly used to describe radionuclide transfer to plants, namely concentration ratios (C_r) and aggregated transfer factors (T_{ag}). All of them are defined for equilibrium condition. It is assumed that radionuclides in plants are in equilibrium with radionuclides in the soil. For terrestrial plants, the C_r is defined as the ratio of the activity concentration of radionuclide in the plant (Bq/kg (DW)) and in soil (Bq/kg (DW)). The C_r values for plants are usually given for the edible parts of the plant:

$$C_r = \frac{\text{Concentration in the plant}\left(\text{Bq/kg}\ \ (\text{DW})\right)}{\text{Concentration in the soil}\left(\text{Bq/kg}\ \ (\text{DW})\right)} \tag{4.2}$$

Thus, all C_r values presented in this section are expressed on a plant dry weight basis according to Eq. (4.2), except where otherwise stated.

The definition of the C_r as a constant, rather than a function, assumes that the concentration in plants increases linearly with increasing substrate concentrations. The linearity assumption infers that the C_r is the slope of the linear relationship of the plant concentration as a function of the soil concentration. The implicit use of the linear regression approach is unsatisfactory if the data are log-normal rather than normal [4.40]. In a review paper, Williams [4.41] reported two power functions which predicted a decreasing C_r for Ra as a function of substrate Ra concentration. Sheppard and Evenden [4.42] critically evaluated the validity of the linear relationship of the plant concentration as a function of the soil concentration and found that generally linearity was obtained only after log-transformation of the data which indicated that calculated C_r would tend to be higher at lower soil concentrations and lower at high soil concentrations.

The limitation of the linearity assumption has been extensively discussed by Simon and Ibrahim [4.32]. They suggested that the dependence of the Ra C_r on substrate concentration is explained in the same way as uptake of calcium and other alkaline earth ions which increase asymptotically as a function of substrate concentration toward a plateau value which may indicate saturation of the binding sites on the root surface, thus limiting the uptake rate. Although the Ra concentration in the substrates may never approach the value required for the saturation of the binding sites on roots, the concurrent presence of high concentrations of calcium and other alkaline earths in the soil solution would contribute to the saturation of the binding sites. Following a compilation of combinations of plant and substrate concentrations from the literature, Simon and Ibrahim [4.32] found that it could be globally inferred that the ratio of the plant uptake to the substrate concentration, which is equivalent to the C_r, is a function that decreases with increasing substrate concentration because of these saturation phenomena. Similarly, Madruga et al. [4.43] stated that for trees growing on U tailing dams, the plant uptake response to the total Ra concentration in the tailings is a non-linear function, tending, however, to a linear relationship at higher U concentrations in the tailings. Contrary to these findings, Blanco Rodríguez et al. [4.44], studying the activity concentrations in different herbaceous plants and substrates collected in a granite zone located near a disused U mine, found that the linearity assumption for ^{226}Ra can be considered valid. Blanco Rodríguez et al. [4.45] set up a hydroponics experiment with sunflower as a test plant, with the intention of testing whether the linearity assumption is valid when the radionuclide concentration in the soil solution and not the total soil concentration is considered. For the ^{226}Ra range covered (1–100 Bq/L) the linearity assumption was found valid.

Another concept, namely that of aggregated transfer factor, has been developed to deal with natural and semi-natural transfers from soil to plants or animals. The concept of T_{ag} is adopted as a reasonable empirical measure to normalize radionuclide accumulation in natural and semi-natural products regardless of variations in the vertical radionuclide distribution and availability in the soil profile, which greatly depends on the site.

$${}_{ag} \qquad \frac{\text{Concentration in the plant}\left(\text{Bq/kg}\left(\text{DW}\right)\right)}{\text{Activity per unit area in the soil}\left(\text{Bq/m}\right)} \tag{4.3}$$

T_{ag} encompasses many processes including food chain transfers, root uptake, soil adhesion, direct soil ingestion, etc. It may have lower variation in the case of transfers from soil because it may overcome the effects of the differences in soil bulk density between organic and mineral soils.

4.2.2.2. Proposed best estimates for radium concentration ratios

Although the C_r concept is a useful tool to predict food chain transport, the usefulness of a single C_r to predict the concentration in vegetables or grain from the concentration in soil is limited when the value is associated with a high variability, as occurs for Ra. It was suggested that a reasonable approach would be to calculate a C_r for each main crop type or, if sufficient data exist, alternatively for each main crop type and each main soil type. This approach was followed by subsequent data compilations.

IAEA TRS 364 [4.29] proposed C_r values for a number of crop groups. The best estimates proposed were 1.2×10^{-3} kg/kg for cereals, 4.9×10^{-2} kg/kg for green vegetables, 7×10^{-3} kg/kg for legumes, 1.6×10^{-2} kg/kg for root crops, 1.1×10^{3} kg/kg for tubers, 8×10^{-2} kg/kg for grasses and 6.1×10^{-3} kg/kg for tomatoes. Hence a 100 fold difference in C_r Ra between crop groups was observed. The IAEA [4.4] engaged in an update of its 1994 handbook on parameter values [4.29] and new best estimates for C_r Ra were proposed. Derivations in the IAEA 2010 compilation and its supporting report [4.12] are generally a factor of 2 higher than the IAEA 1994 estimates. The derived generic C_r (all crop groups and soil types) was estimated at 3×10^{2} kg/kg (geometric mean, GM; geometric SD = 7) with a range in observed values of 5 orders of magnitude. Pastures/grasses, leafy vegetables, root crops, fodder and herbs showed the highest C_r

estimates ($4 \times 10^{-2} - 10^{-1}$ kg/kg); cereals, non-leafy vegetables, legumes, tubers and fruits showed the lowest ($2 \times 10^{-3} - 2 \times 10^{-2}$ kg/kg) (Table 4.2). Variation within a crop group was 1–3 orders of magnitude, and significant differences in C_r values between crop groups were rarely observed [4.46]. Recorded C_r for maize was tenfold less than for the other cereals. C_r for cereal or maize straw was a factor of two lower than the corresponding grains. Hardly any significant effect of soil type on Ra C_r was observed (Table 4.2). No significant dependency of C_r-Ra on experimental conditions (potted soil, lysimeter, field), contamination history (artificial contamination, natural Ra) or climate (temperate regions, tropical or sub-tropical regions) could be established from the data compiled [4.46].

IAEA TRS 472 [4.4] estimates are generally within a factor of 2 in agreement with C_r Ra values derived by Brown and Simmonds [4.47] and Ewers et al. [4.48]. C_r (geometric mean) values for Ra proposed by Sheppard et al. [4.49] were (in kg/kg dm basis) as follows: 3×10^{-2} for cereals, 2×10^{-2} for vegetables, 1.8×10^{-2} for root crops, 4×10^{-2} for fruits, berries and nuts, and 10^{-2} for forages. These values are 3–4 times higher than the newly derived IAEA values for cereals and fruits, comparable for forages and vegetables, and lower (factor of 4) than for for root crops. Sheppard et al. [4.28, 4.49] suggested a global C_r value for human food crops of 1.7×10^{-2} kg/kg.

Sheppard et al. [4.28] also collected C_r values for native forage and vegetation. C_r values derived were 0.1 for native browse, 0.1 for forages, 0.78 for shrubs, 0.1 for trees and 0.3 for lichens and mosses. The derived generic C_r value for native forage and vegetation was 5×10^{-2} (GSD 6.4, N = 624kg/kg).

Sheppard et al. [4.28] observed that ^{228}Ra seemed to be 5 times more bioavailable than ^{226}Ra for natural vegetation at Canadian radiation background sites. However, Linsalata [4.50] did not find a significant difference in ^{226}Ra and ^{228}Ra C_r averaged for a series of crops grown at the Poços de Caldas plateau (Brazil). Within the IAEA [4.4] compilation (details reported by Vandenhove et al. [4.46]), there were a number of studies where both ^{226}Ra and ^{228}Ra were monitored [4.50–4.52]. For a large number of crops (maize, brown beans, cassava, carrot, lettuce, grasses, herbs) no significant difference in C_r for was recorded for either isotope.

Most of the C_r values discussed here are for food or forage crops important for human dose assessment. C_r values for native plants have generally been less reported, except for plants growing in the vicinity of U mining and milling sites or high background areas. Simon and Ibrahim [4.32] presented C_r values for sagebrush, grasses and herbs ranging from 0.05 to 0.7 kg/kg. C_r values for natural crops in high background areas were generally in the range of 0.001 to 0.07 kg/kg. For soils originating from a disused U mining area, Vera Tomé et al. [4.53] reported C_r values for prairie grass ranging from 0.10 to 0.50 kg/kg. Lower C_r

values were reported by Chen et al. [4.54] for soils contaminated with U mine tailings (C_r = 0.0021 kg/kg for ryegrass and 0.034 kg/kg for clover).

The IAEA [4.4] assembled C_r values for fauna and flora. Mean values (arithmetic mean, ratio of Bq/kg plant on a fresh weight basis and Bq/kg dry soil, ±SD) were 0.19 (0.66) for grasses and herbs, 1.7 (3.4) for lichens and bryophytes, 1.00 (1.6) for shrubs and 6.8×10^{-4} (7.5×10^{-4}) for trees. The mean C_r value for grasses and herbs is in good agreement with those for agricultural and semi-natural ecosystems (Table 4.2 [4.12]). Lichens and bryophytes show a very high C_rs (range 0.065–23). The fern *Dicranopteris linearis*, considered a hyperaccumulator of Ba, and a number of rare earths and heavy metals, was also a strong accumulator of Ra with C_r as high as 4 kg/kg (DW) [4.55].

TABLE 4.2. RADIUM SOIL TO PLANT CONCENTRATION RATIO FOR CROP GROUPS, CROP COMPARTMENTS AND CROP/SOIL COMBINATIONS (KG/KG DW)

Plant group	Plant compartment	Soil	*N*	GM	GSD	Min	Max
All		All	549	3.3×10^{-2}	7.1	1.1×10^{-5}	3.3
Cereals	Grain	All	24	1.7×10^{-2}	1.2×10^{1}	8.0×10^{-5}	6.7×10^{-1}
		Loam	7	2.9×10^{-2}	9.70	8.0×10^{-4}	6.7×10^{-1}
		Clay	10	3.9×10^{-2}	9.88	2.4×10^{-4}	5.0×10^{-1}
	Stems and shoots	All	20	3.6×10^{-2}	4.78	1.6×10^{-3}	4.3×10^{-1}
		Loam	10	5.2×10^{-2}	4.44	7.2×10^{-3}	4.3×10^{-1}
Maize	Grain	All	28	2.4×10^{-3}	5.4	1.2×10^{-4}	1.1×10^{-1}
		Loam	4	1.7×10^{-3}	1.8	9.0×10^{-4}	3.0×10^{-3}
		Clay	16	1.4×10^{-3}	4.8	1.2×10^{-4}	1.1×10^{-1}
	Stems and shoots	All	6	1.8×10^{-2}	5.2	9.6×10^{-4}	8.5×10^{-2}
Leafy vegetables	Leaves	All	73	6.6×10^{-2}	3.8	1.8×10^{-3}	5.9×10^{-1}
		Loam	10	1.2×10^{-1}	2.5	1.6×10^{-2}	4.4×10^{-1}
		Clay	20	4.0×10^{-2}	4.5	1.8×10^{-3}	4.2×10^{-1}
		Organic	9	4.9×10^{-2}	2.1	2.0×10^{-2}	1.4×10^{-1}
Non-leafy vegetables	Fruit, heads, berries, buds	All	41	1.2×10^{-2}	5.2	2.4×10^{-4}	3.4×10^{-1}

TABLE 4.2. RADIUM SOIL TO PLANT CONCENTRATION RATIO FOR CROP GROUPS, CROP COMPARTMENTS AND CROP/SOIL COMBINATIONS (KG/KG DW) (cont.)

Plant group	Plant compartment	Soil	*N*	GM	GSD	Min	Max
		Sand	3	2.2×10^{-3}	2.1	1.1×10^{-3}	5.0×10^{-3}
		Loam	4	4.8×10^{-2}	5.6	6.9×10^{-3}	3.4×10^{-1}
		Clay	17	2.2×10^{-2}	2.8	3.9×10^{-3}	2.1×10^{-1}
	Stems and shoots	All	13	6.1×10^{-2}	6.4	6.7×10^{-3}	1.8
Leguminous vegetables	Pods	All	38	1.0×10^{-2}	5.5	3.2×10^{-4}	2.6×10^{-1}
		Loam	12	9.8×10^{-3}	4.5	4.8×10^{-4}	8.7×10^{-2}
		Clay	15	9.3×10^{-3}	4.2	8.0×10^{-4}	1.1×10^{-1}
	Shoots	All	18	2.8×10^{-2}	1.1×10^{1}	1.1×10^{-5}	1.5
		Loam	6	1.1×10^{-2}	3.2×10^{1}	1.1×10^{-5}	1.1×10^{-1}
Root crops	Roots	All	54	3.9×10^{-2}	4.1	2.0×10^{-3}	3.8×10^{-1}
		Sand	3	$4.8 \times E^{-3}$	2.3	2.0×10^{-3}	1.1×10^{-2}
		Loam	8	9.1×10^{-2}	1.9	2.9×10^{-2}	2.0×10^{-1}
		Clay	23	3.2×10^{-2}	2.9	3.2×10^{-3}	2.2×10^{-1}
	Stems and shoots	All	22	7.1×10^{-2}	4.6	2.5×10^{-3}	7.1×10^{-1}
		Loam	6	1.4×10^{-1}	5.6	9.6×10^{-3}	7.1×10^{-1}
Tubers	Tubers	All	44	8.6×10^{-3}	5.1	2.4×10^{-4}	6.2×10^{-1}
		Loam	8	1.2×10^{-2}	1.1×10^{1}	2.4×10^{-4}	6.2×10^{-1}
		Clay	24	5.4×10^{-3}	2.5	1.3×10^{-3}	8.0×10^{-2}
	Stems and shoots	All	6	1.6×10^{-1}	2.2	4.3×10^{-2}	3.3×10^{-1}
Herbs	Herbs	All	20	6.9×10^{-2}	4.5	5.3×10^{-3}	3.3
Fruits	Fruits	All	12	1.2×10^{-2}	3.7	1.4×10^{-3}	1.7×10^{-1}
Other	Sunflower-3/ peanut-1	All	4	4.2×10^{-1}	3.0	8.5×10^{-2}	1.1
Grasses	Stems and shoots	All	62	1.3×10^{-1}	4.0	3.6×10^{-3}	1.6

TABLE 4.2. RADIUM SOIL TO PLANT CONCENTRATION RATIO FOR CROP GROUPS, CROP COMPARTMENTS AND CROP/SOIL COMBINATIONS (KG/KG DW) (cont.)

Plant group	Plant compartment	Soil	*N*	GM	GSD	Min	Max
		Sand	24	1.4×10^{-1}	4.2	5.3×10^{-3}	1.6
		Loam	14	2.6×10^{-1}	2.0	9.6×10^{-2}	7.2×10^{-1}
		Clay	3	4.2×10^{-2}	1.5	2.7×10^{-2}	6.1×10^{-2}
Pastures (natural)	Stems and shoots	All	42	7.1×10^{-2}	7.6	5.1×10^{-5}	1.6
		Sand	3	8.0×10^{-3}	3.8	1.8×10^{-3}	2.3×10^{-2}
		Loam	6	8.8×10^{-3}	1.9×10^{1}	5.1×10^{-5}	1.1×10^{-1}
Leguminous fodder	Stems and shoots	All	16	1.7×10^{-1}	3.1	3.4×10^{-2}	1.5
		Sand	5	1.7×10^{-1}	2.5	8.0×10^{-2}	5.6×10^{-1}
		Loam	8	1.2×10^{-1}	3.9	3.4×10^{-2}	1.5

Note: N Number of entries; GM Geometric mean; GSD Geometric standard deviation.

4.2.2.3. Soil and plant characteristics affecting the radium soil to plant concentration ratio

The previous section shows clearly that there is a large variability in observed C_r values. An obvious intial reason for this variability is the dependency of the C_r value on soil concentration, as explained earlier. However, the availability of an element from soils for plant uptake is further controlled by a large number of physical, chemical, biological and climate factors, by crop management practices and by the experimental conditions under which the soil to plant concentration ratios were obtained.

There are several distinct processes which must take place for plant uptake to occur. The first is the release of the ions from the solid phase of the soil to the soil solution, followed by the movement of these ions to locations where roots are present. Concepts such as availability are helpful in describing the processes and mechanisms that determine the potential of ions for plant uptake and are defined as those belonging to a pool which contributes to uptake by plants grown on soil [4.32]. The major factor governing availability to plants from soil is the solubility of the element associated with the solid phase. However, the degree of availability in the soil solution is also dependent on the soil–plant interaction. For example, the root system may alter the pH of the soils adjacent to it [4.56]. Competitive effects at, and exchange of ions onto, the root surface, transport across the root membranes and the subsequent translocation into the plant tissue complete the process. The reviews of Simon and Ibrahim [4.32] and Sheppard et al. [4.49] show how few studies were conducted that allowed a mechanistic explanation of observed soil to plant concentration ratios.

The following paragraphs highlight some studies where the effect of soil and plant parameters on the Ra soil to plant transfer was evaluated.

Effect of soil texture, soil organic matter and soil cation exchange capacity.

As a bivalent cation, Ra has a high affinity for the regular exchange sites of soil. Kirchmann et al. [4.57] determined an inverse relationship between the log of the ^{226}Ra content in plants and the amount of sorptive material in soil. Lauria et al. [4.58] reported a significant inverse correlation between C_{r}_Ra and the soil CEC. According to Simon and Ibrahim [4.59], organic matter adsorbs about ten times as much Ra as clay, which is more adsorptive than other soil minerals. Vandenhove and Van Hees [4.17] found, in a potted soil experiment with prairie soils, that log-C_{r} for grass and clover were strongly correlated with the soil CEC and with soil organic matter.

Evaluating the overall effect of soil texture on the soil to plant transfer of Ra for the IAEA compilation [4.4, 4.46], clay (1.71×10^{-2} kg/kg, GSD 6.65) and organic soils (1.63×10^{-2} kg/kg, GSD 16.9) showed the lowest C_{r} values and sand (4.39×10^{-2} kg/kg, GSD 7.88) and loam soil (4.29×10^{-2} kg/kg, GSD 7.54) the highest, yet the difference was only fourfold and only the C_{r} for clay was significantly different from the C_{r} for sand and loam. This is explained by the fact that within each soil group many crop groups were assembled and C_{r} values ranged over 4 orders of magnitude. A significant effect of soil texture or organic matter content on C_{r}_Ra was only observed for a few crop groups (non-leafy vegetables, root crops) (Table 4.2 [4.12]). Moreover, following regression analysis using Ref. [4.4], clay content and C_{r}_Ra were not correlated (neither overall nor for specific crop groups). Though it was not possible to derive a significant correlation between organic matter content and C_{r}_Ra considering all crop groups, a significant negative dependency of C_{r}_Ra on OM content was found for legumes ($R^2 = 0.42$), leguminous fodder ($R^2 = 0.62$) and natural pastures ($R^2 = 0.27$) [4.46].

Effect of soil calcium content.

It has been documented that alkaline earth metals may compete for adsorption binding sites on the root surface. In the presence of high soil concentrations of alkaline earth cations, the uptake of Ra may be suppressed due to adsorption competition. Some authors have referred to a membrane discrimination mechanism [4.12]. The observed ratio (OR= Ra/Ca in plants, or Ra/Ca in soil) has been documented to be less than unity in plants, suggesting the existence of a discrimination mechanism of membranes in ion uptake from soils to plants. Several authors found that total soil bivalent cation concentration [4.12] and exchangeable Ca and Mg [4.60] suppressed Ra uptake. In a greenhouse experiment with three different soils artificially contaminated with Ra, Vandenhove et al. [4.61] found a significantly negative dependence (power) of C_r Ra for clover and ryegrass in the concentration of Ca and Mg in soil solution. Subsequently, Vandenhove and Van Hees [4.17] found a significant negative relation between log-C_r and soil solution calcium concentration for both ryegrass and clover, but not with the total bivalent cation concentration ($Ca^{2+} + Mg^{2+}$) in the soil solution. However, Vasconcellos et al. [4.62] and Lauria et al. [4.58], who studied Ra transfer in high natural background areas and at conventional and organic farms, respectively, argued that the exchangeable Ca in soils did not seem to influence Ra uptake by plants in a defined way.

Hypothesizing that the Ra soil to plant transfer would be reduced by the soil's sorption power (CEC, soil factor) and the concentration of competitive cations in the soil solution (plant factor: competition at root surface for uptake), Vandenhove and Van Hees [4.17] showed that log-C_r could be well predicted from the inverse product of $1/(\mathrm{CEC}\cdot[Ca^{2+} + Mg^{2+}])$ with $[Ca^{2+} + Mg^{2+}]$, the concentration of $Ca^{2+} + Mg^{2+}$ in the soil solution. Hence, the combined parameter $1/\ (\mathrm{CEC}\ \ [Ca^{2+} + Mg^{2+}])$ seems to be a better way to predict Ra C_r than the single parameters CEC and $[Ca^{2+} + Mg^{2+}]$.

Effect of soil pH and soil P status.

Gerzabek et al. [4.60] conducted lysimeter studies to determine the uptake of ^{226}Ra by agricultural crops and reported significant negative correlations between C_r and pH. The pH effect was explained by the lower Ra availability with increasing pH [4.63]. For the IAEA compilation [4.4, 4.46], a significant negative dependency of C_r Ra on pH was only observed for leguminous fodder and grasses. No significant pH effect on C_r Ra was observed by Vandenhove and Van Hees [4.17].

Ra uptake has been reported to be influenced by soil P content [4.64]. Vandenhove and Van Hees [4.17] found a weak correlation between the ryegrass and clover C_rs and total soil P. No correlation was found with available P or P concentration in the soil solution. In the study of Million et al. [4.65], P nutrition did not affect Ra uptake.

Relation with plant Ca and Ba content

The influence of plant calcium content on Ra uptake is not clear. Several authors reported a positive correlation between shoot Ca content and shoot Ra content. Linsalata et al. [4.66] found that C_r Ra was positively correlated with plant Ca content in a field study in an area of enhanced natural radiation (Fig. 4.4). Similarly, Kopp et al. [4.67] and Million et al. [4.65] found a positive correlation between plant Ca content and C_r Ra. However, Vasconcellos et al. [4.62] and Vandenhove and Van Hees [4.17] both failed to detect a significant correlation between plant Ca content and Ra uptake.

Blanco Rodríguez et al. [4.64] found a strong positive correlation between the Ba and Ra content of grass pasture samples, which was explained by their similar chemical behaviour. Barium was considered a good tracer for Ra given the highly significant linear correlation between the C_r Ra and C_r Ba for ryegrass

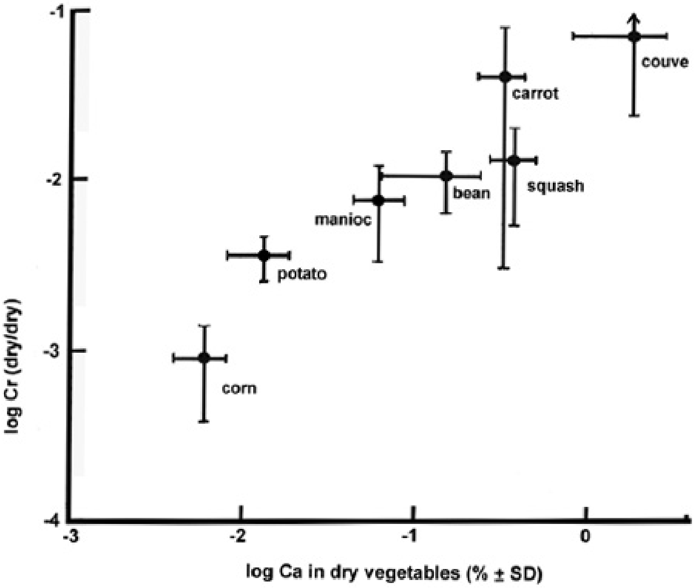

FIG. 4.4. Relationship between the mean Ra C_r values for vegetables and their Ca content (from Linsalata et al. [4.66]). Error bars are arithmetic standard deviations.

and clover grown on artificially contaminated prairie soils [4.61]. Tagami and Uchida [4.68] found a strong correlation between the Ba and ^{226}Ra concentrations for edible parts of plants if the Ba and Ra concentrations in soil were within the normal range (84–960 mg/kg for Ba and 8–100 Bq/kg for ^{226}Ra). Similarly, Uchida and Tagami [4.69] observed that concentration ratios for Ra and Ba for rice were significantly correlated. A stronger correlation was observed between C_r-Ra and C_r-Ba than between C_r-Ra and C_r-Ca for ferns [4.55]. These examples show that Ba can be considered a good tracer for Ra.

4.2.2.4. Dynamic description of the C_r

Simon and Ibrahim [4.32] called for the C_r to be treated as a function rather than as a constant. Subsequently, the influence of soil characteristics, crop growth and the kinetics of Ra movement was studied by Vandenhove and Van Hees [4.17]. They calculated total Ra flows, taking into account Ra concentration in the soil solution, total water use by plants, shoot Ra concentrations and biomass production. Hypothesizing that the Ra concentration in the soil solution is in the readily available pool for uptake and that evaporation is the driving force for uptake, the Ra flow (Bq) to the roots could then be estimated by multiplying both parameters. Following the hypothesis, this flow can be expected to be significantly related to the total Ra incorporated in the plant shoot (Bq, total uptake defined as the biomass yield (kg) × the Ra concentration in the shoots (Bq/kg)). The Ra flow accounted for 61–83% of the variation in total measured Ra uptake. Additionally accounting for potential competition effects for uptake induced by the presence of the bivalent cations Ca^{2+} and Mg^{2+} in the soil solutions, the Ra uptake was predicted by the ratio of the Ra flow and the concentrations of those bivalent cations in soil solution. This resulted in even better estimations of the total Ra uptake with 70% (ryegrass) and 92% (clover) of the variation accounted for.

4.2.2.5. Distribution of radium between plant tissues and chemical forms of Ra in plants

A decreasing gradient from the oldest to youngest organs and towards the apex of the plant has been observed for Ra. Thus, a number of studies have reported radium activity concentrations decreasing from roots to stems and from stems to shoots and leaves in many different plant types under different growing conditions [4.32]. Radium was preferentially retained by the roots and discriminated against during subsequent transport to the shoots of barley, peas and maize grown in nutrient solutions [4.70]. Markose et al. [4.62] found C_r values for tomatoes showing the following order: roots > stem > fruits. Blanco Rodríguez et al. [4.64] reported that transfer to fruits of *Eucalyptus* *camaldulensis, Cytisus multiflorus* and *Quercus suber* grown in a disused U mine located in the Extremadura region was always lower than transfer to leaves. Similarly, higher C_rs were observed for straw than for grain, for pea shoots than for pods and for shoots of non-leafy vegetables than for their fruits [4.4]. The existence of an acropetal gradient suggests that Ra is not metabolically active in plants. Kirchmann et al. [4.71] determined that Ra deposited in leaves was not redistributed during plant growth. Linsalata et al. [4.66] also observed that calcium exhibited little retranslocation once delivered to a specific organ of a plant and that this appeared to be true for Ra as well. After being intercepted by the plant, it remains where it is initially located without further distribution and does not enter into the metabolic cycle. This may explain the observation of Soudek et al. [4.72] that within a vegetation growth season, Ra activity concentrations in the leaves of *Betula pendula, Sambucus nigra* and *Alnus glutinosa* sampled at an old U tailing dump increased as it was not tranported back, e.g. by the phloem. The transport of Ra by the transpiration stream may explain the generally high C_r values for the leaves of leafy vegetables (e.g. Table 4.2) as these plant tissues have a high transpiration rate.

The chemical form of Ra in plants may determine its mobility within the plant. However, the exact chemical speciation of Ra in plants has not yet been identified. Some chemical speciation studies were presented by Simon and Ibrahim [4.32]. These extraction studies highlight that Ra was mostly present in an available form.

4.2.3. Radium transfer to animals

4.2.3.1. Transfer to agricultural animals

Radium behaves in a similar manner to calcium, which is a major metabolic element. Similar patterns of metabolism for ^{226}Ra and Ca have been shown for rabbits [4.73] and dairy cows [4.74]. Moreover, distribution studies on animals have indicated that ^{226}Ra is predominantly located in Ca rich tissues [4.75]. Ca metabolism would therefore be expected to influence Ra transfer to animals, as evidenced by the reduced accumulation of ^{226}Ra caused by increased Ca concentrations in the diet [4.75].

Absorption

The ICRP recommends a fractional absorption value of 0.2 for Ra (and Ba) [4.76], which is slightly lower than the value of 0.3 of its analogues, calcium and strontium. Data for Ra gastrointestinal absorption in ruminants have not been reported, but fractional gut absorption values for ruminants of 0.055 for Ba and 0.11 for Sr are reported in Howard et al. [4.77].

Transfer to animal food products

The major pathway for Ra transfer to animals is through ingestion of feed and water [4.78] and Ra intake is highly variable. As Ra behaves similarly to other alkaline earth elements such as Ca, Sr and Ba, it mainly accumulates in bone so the few reported data show low transfer to animal products, which form important parts of the human foodchain such as meat.

The transfer coefficient often used for quantifying radionuclide transfer to both milk (F_m, d/L or d/kg) and meat (F_f, d/kg) is the equilibrium ratio of the radionuclide activity concentration in milk/meat to the daily dietary radionuclide intake [4.4, 4.12, 4.79]. Reported values for the transfer coefficient in animal food products in TRS 472 [4.4] are shown in Table 4.3 [4.12] and are based on four sets of data for cow's milk [4.74, 4.80, 4.81, 4.82] and one for beef [4.50].

TABLE 4.3. TRANSFER COEFFICIENTS FOR RADIUM TRANSFER TO FOODSTUFFS FROM ANIMALS

Animal product	Transfer coefficient (d/L and d/kg)				
	N	GM	GSD	Min	Max
Cow's milk	11	3.8×10^{-4}	2.3	9.0×10^{-5}	1.4×10^{-3}
Beef	1	1.7×10^{-3}	n/a	n/a	n/a

The transfer coefficient for Ra to milk is lower than that for the essential element Ca, which is 1.0×10^{-2} d/kg, but is more similar to that for Sr of 1.3×10^{-3} d/kg and Ba, which is 1.6×10^{-4} d/kg [4.4, 4.12].

The transfer coefficient for Ra to beef is higher than that for milk, and this is consistent with the reference ^{226}Ra activity concentration values for milk and meat of 15 and 5 Bq/kg, respectively. As for milk, the transfer coefficient for Ra to beef is lower than that for the essential element, Ca, which is 1.3×10^{-2} d/kg, but is similar to that for Sr, of 1.3×10^{-3} d/kg, and Ba, which is 1.4×10^{-4} d/kg [4.4, 4.12].

An alternative method described in TRS 472 [4.4] for quantifying transfer from herbage to animal products is the concentration ratio, C_r, which is the equilibrium ratio of the radionuclide activity concentration in the animal food product (FW) divided by the radionuclide concentration in the feed (dry matter). C_r values for Ra were not reported in TRS 472. C_r values for milk varying from 3.7×10^{-3} to 14×10^{-3}, with an unweighted mean of 5.5×10^{-3}, were reported in a review by Watson et al [4.83]. Recent data from Nordic countries gives a higher GM C_r value of 2.3×10^{-2} d/kg based on data for both ^{226}Ra and ^{228}Ra [4.84]. The latter value used measured values for both ^{226}Ra and ^{228}Ra activity concentrations in feed and milk; the milk activity concentrations for ^{226}Ra were consistently low (at $<4.0 \times 10^{-3} - 3.0 \times 10^{-1}$Bq/kg) compared with most values reported by UNSCEAR (Table 3.31). A higher C_r for Ra in beef of 1.8×10^{-1} with a standard deviation of 3.8×10^{-1} ($n = 11$) was reported in TRS 472, based on four data sources [4.50, 4.85–4.88]. In contrast, using the reference concentration for ^{226}Ra in milk and meat from UNSCEAR and comparing it with the ((DW)) mean of that in grassy vegetation, C_r values of 1 and 3, respectively, are derived. However, these latter ratios are based on unassociated samples and are likely to be less reliable than the lower value reported in TRS 472 [4.4].

Transfer to extensive terrestrial animal wildlife groups and food products.

The transfer of Ra to extensive food products such as game species has not been quantified in TRS 472 or TECDOC 1616 [4.4, 4.12].

The transfer of radionuclides to wildlife has recently been compiled in a new TRS [4.88] in which the transfer to whole terrestrial organisms has been reported for a few animal species as concentration ratios between the FW whole organism (excluding gut, feathers and pelt) of terrestrial animals and soil (dry matter, (DW)) (Table 4.4, [4.88]). The definition of $C_{r\ \text{wo-soil}}$ for terrestrial ecosystems at equilibrium is:

$$C_{r\,\text{wo}-\text{soil}} = \frac{\text{Activity concentration in whole organism}\left(\text{Bq/kg FW}\right)}{\text{Activity concentration in soil}\left(\text{Bq/kg}\right)\left(\text{DW}\right)} \qquad (4.4)$$

The $C_{\text{r wo-soil}}$ values do not include shell, antlers, skin and gut contents, but do include bone. The Cr_{wo} values for Ra transfer to arthropods are higher than those for birds, mammals and gastropod molluscs. There is little difference in transfer of Ra in either birds or mammals between carnivorous and herbivorous species. These values are not directly comparable to those given above for beef as the Cr are for the whole organism (notably including bone), and the denominator is soil rather than ingested feed.

The Ra Cr $_{\text{wo-soil}}$ values for the different mammal categories are consistently lower than the equivalent values for Sr (which varies from 8.6×10^{-1} to 1.8, with a mean for all mammals of 1.6).

No Ra Cr values are available for Rangifer species; a relatively high Sr Cr $_{\text{wo-soil}}$ value of 6.5 was reported for Rangifer reindeer in the new TRS [4.88].

TABLE 4.4. TRANSFER OF RADIUM TO DIFFERENT WILDLIFE GROUPS

Wildlife group		Cr wo-soil			
		GM	SD	Min	Max
Arthropod	27	2.1×100	2.5×100	1.0×10^{-2}	8.9×100
Bird	48	2.1×10^{-2}	2.8×100	2.1×10^{-3}	2.0×10^{-1}
Bird — carnivorous	16	3.1×10^{-2}	2.7×100	2.7×10^{-3}	2.0×10^{-1}
Bird — herbivorous	25	2.1×10^{-2}	2.6×10^{0}	2.1×10^{-3}	1.9×10^{-1}
Mammal	84	1.7×10^{-2}	4.1×10^{0}	5.7×10^{-5}	7.6×10^{-1}
Mammal — carnivorous	25	4.1×10^{-2}	1.6×10^{0}	1.5×10^{-2}	1.2×10^{-1}
Mammal — herbivorous	45	6.1×10^{-3}	3.8×10^{0}	5.7×10^{-5}	2.0×10^{-1}
Mammal — marsupial	9	1.3×10^{-1}	2.9×10^{0}	5.5×10^{-3}	7.6×10^{-1}
Mollusc — gastropod	10	3.4×10^{-2}	2.3×10^{0}	2.5×10^{-2}	1.4×10^{-1}

Overall,the transfer of Ra to animals is similar to that for Sr and Ba and lower than that for the essential element Ca.The relative importance of animal products as dietary sources of Ra is low compared with that of plants.

4.3. FRESHWATER

4.3.1. Groundwater

4.3.1.1. Ra concentrations in groundwaters

The most abundant Ra isotope in groundwater is ^{226}Ra. Concentrations of ^{226}Ra in groundwater vary widely (Figure 4.5). Low salinity groundwaters from a wide range of aquifer lithologies were found to have a ^{226}Ra concentration of 1.2–1600 Bq L^{-1}, generally with comparable activities of ^{228}Ra (e.g. Ref. [4.89]). A wide survey of drinking water wells across the United States found a mean ^{226}Ra of 0.014 Bq L^{-1}, and a maximum of 0.63 Bq/L [4.90]. A very broad general correlation was found with ^{228}Ra, which had a maximum concentration of 2.68 Bq L^{-1}. A better correlation was found with ^{224}Ra, which had a maximum concentration of 2.72 Bq L^{-1}, though most wells had <0.04 Bq L^{-1}. Wells in bedrock aquifers in the Helsinki region had ^{226}Ra concentrations ranging from <0.004 to 9.47 Bq L^{-1}, with a mean of 0.30 Bq L^{-1}, with substantially higher values than in dug wells from the region, which had a mean of 0.01 Bq L^{-1} [4.91]. In this area, values of ^{228}Ra up to 0.570 Bq L^{-1} were found [4.92]. Since natural U has an activity ratio of (^{238}U/^{235}U) = 21.8, ^{223}Ra concentrations are always much lower than the other Ra isotopes.

Groundwaters generally have Ra concentrations that broadly correlate with salinity or total dissolved solids (TDS) [4.93], although as shown in Fig. 4.5 [4.94–4.98], there is little correlation for concentrations of ^{226}Ra <1 Bq/L. For comparison, the USEPA standard for combined activities of ^{226}Ra and ^{228}Ra is 0.185 Bq/L. Using the USEPA secondary drinking water standard for TDS of 500 mg/L as a benchmark, it can be seen that most groundwaters under this limit have ^{226}Ra concentrations below ~1 Bq/L, although some areas, such as groundwaters in Jordan, have consistently high values [4.96].

4.3.1.2. Natural sources of Ra in groundwaters

Weathering. Breakdown of minerals containing Ra can provide a continuing subsurface supply throughout an aquifer. Primary minerals containing U and Th have Ra isotopes in secular equilibrium with the decay series parents, as will secondary phases that are sufficiently old (>10^{5} years; see Chapter 2). In this case, nuclides may be added with equal activities, e.g. with (^{238}U/^{226}Ra) = 1. Very young phases that are rich in ^{232}Th and also incorporate ^{230}Th from the ^{238}U series will have ^{224}Ra and ^{228}Ra approaching secular equilibrium with ^{232}Th, but may have little ^{226}Ra, while those over ~8,000 a will have (^{230}Th/^{226}Ra) = 1. However, such phases will have diminishing ^{230}Th activities over timescales of the order

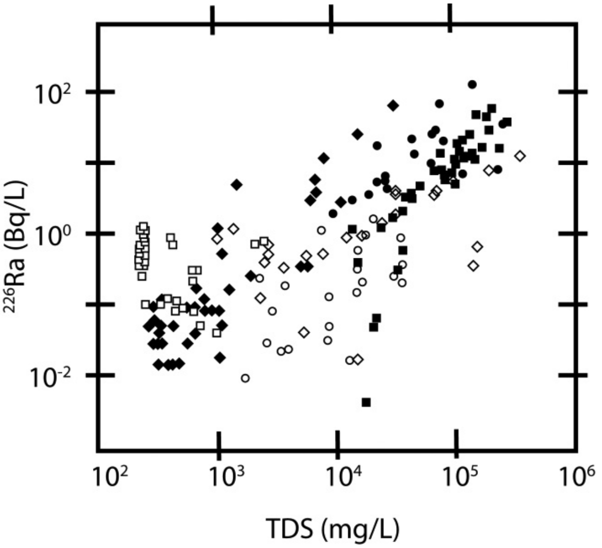

FIG. 4.5. 226Ra concentrations in groundwaters. Data from Manitoba, Canada ([4.93] filled diamonds,) Israel ([4.94] open diamonds), Japan ([4.95] open circles), Jordan ([4.96] open squares), central USA ([4.97] filled circles) and ([4.98] filled squares)).

of the half-life of ^{230}Th. Similarly, phases rich in Ra, such as sulphates, must be sufficiently young (on the scale of the half-life of ^{226}Ra) to still contain Ra. Also, while ^{238}U and ^{235}U will be similarly distributed within aquifer phases along with their daughters ^{226}Ra and ^{223}Ra, ^{232}Th may be in different phases along with ^{224}Ra and ^{228}Ra. Thus, Ra isotopes in the different decay chains may be released at different rates. Where Ra concentrations correlate with another element that is released by weathering, the input of Ra predominantly by weathering might be inferred; e.g. a correlation of Ra with La might be an indication of weathering of monazite ((REE, Th)PO_4) [4.99]. However, correlations between two elements may also reflect variations in the processes that remove both elements. Conversely, nuclides that are released together will not necessarily be correlated within groundwaters due to different removal rates.

Recoil. Another important source for U/Th series nuclides in aquifers is alpha recoil [4.100].Each alpha decay occurs with sufficient energy that the resulting daughter nuclide is propelled in a random direction for a distance of ~20 nm in most U/Th-bearing minerals. When such a daughter atom crosses the mineral–water interface, it can either stop within the groundwater or within another phase from where it can migrate back out through the damaged lattice. This is a purely physical process that is unaffected by groundwater chemistry. The fractions of the radionuclides that are produced within aquifer rocks that are released (ε) are determined by the fraction located within 20 nm of mineral surfaces. Since ^{238}U and ^{235}U may be located in different phases than ^{232}Th, a different fraction of the nuclides in this chain may be recoiled.

Decay of adsorbed and dissolved parent Th isotopes. Decay of parent Th isotopes that are in solution will supply Ra directly to groundwater, although since Th is highly particle reactive it is highly depleted in groundwaters and is largely adsorbed onto aquifer surfaces. Decay of adsorbed Th will recoil Ra directly into the surrounding water or into the underlying mineral, from which it is likely to be readily leached.

Controls on groundwater concentrations

Barite precipitation. The most common mineral that precipitates from groundwater and incorporates Ra is barite [4.101], which commonly controls groundwater Ba concentrations [4.102]. For example, Grundl and Cape [4.103] found freshwater to be saturated in barite and so controlling Ra concentrations in a sandstone aquifer. Langmuir and Melchior [4.101] found that the concentrations of dissolved Ra in some deep brines in north Texas were likely controlled by co-precipitation in barite, as well as in other sulphate minerals such as celestite ($SrSO_4$), due to the high concentrations of sulphate and alkali earth elements. Modelling of the groundwater migration of Ra from a waste site, limited by precipitation in sulphates and carbonates, has been done by Shao et al. [4.104].

Radium concentration can vary considerably even in samples that are saturated with barite (e.g. Kelly [4.105]).The rate of barite precipitation will be controlled by Ba (and sulphate) supply; since Ra is many orders of magnitude less abundant, so changes in its concentration have little effect on the rate of barite formation. Therefore, while changes in the rate of barite precipitation will produce correlations in Ba and Ra concentrations, only variations in Ra supply that will not result in such correlations can occur, even when barite is saturated.

Adsorption. A dominant control on Ra behaviour in many groundwaters is adsorption onto aquifer surfaces.Vengosh [4.96] compiled the available data for sandstone aquifers with low salinity oxic groundwaters and found that Ra did not correlate with either ^{222}Rn (a measure of recoil supply) or total dissolved solids (a measure of weathering supply), and argued that the controlling factor was the extent of secondary phases that effectively adsorb Ra. The most important phases for Ra adsorption are generally Fe and Mn oxyhydroxides and clays. However, it is difficult to predict bulk partition coefficients for aquifer rocks, since the specific surface areas for these phases are generally very heterogeneous. Adsorption and desorption occurs very rapidly, over timescales of seconds to hours [4.101, 4.106].

Groundwater samples, typically either unfiltered or filtered with a ~0.5 μm filter, may contain colloids that have adsorbed radionuclides that enhance migration rates. The compositions of colloids vary widely and include inorganic constituents such as Fe or Mn oxyhydroxides and clay, as well as organic colloids and microorganisms. Colloids typically have large surface areas for complexation and ion exchange reactions, and have been shown to effectively transport a variety of constituents. Ivanovich et al. [4.107] reviewed how this may relate to radionuclide transport, but data are limited. Colloids have been found to carry a large fraction of U in groundwaters [4.108]. Due to the greater reactivity, Th is also likely to be efficiently carried by colloids [4.109]. Ra may be readily attached to other colloids due to its strong affinity to surfaces, and so colloid and particulate transport on clays and iron hydroxides may have a role in Ra transport under some circumstances, although this has not been widely investigated.

Redox environments and pH control. Radium is present in only one oxidation state,as Ra^{2+}, and so is not directly affected" by changes in aquifer redox state. However, other species that have an impact on Ra behaviour can be affected. Under reducing conditions, sulphate ions may be reduced, so that barite saturation is not reached (see the discussion of highly saline waters immediately below). Almeida et al. [4.110] found that groundwaters in Brazil with very low natural pH values of <5 had higher ^{226}Ra and ^{228}Ra concentrations. This was likely due to decreased adsorption on Fe oxyhydroxide surfaces that have a positive charge at such low pH. Such an effect will be seen wherever the pH drops below the zero point of charge of the main adsorbing phases. Also, under anoxic conditions, Fe and Mn phases can dissolve, and so be unavailable as Ra adsorbers. For example, waters in fractured bedrock have Ra concentrations that are significantly higher in anoxic waters that have elevated Fe and Mn concentrations from Fe and Mn oxide dissolution [4.111]. Areas of oxidation and consequent active precipitation of Fe and Mn oxides can change water chemistry and accumulate Ra; the high ^{222}Rn contents of springs in Switzerland were ascribed to near surface mixing between warm anoxic deep waters and oxic waters, creating a Ra rich ^{222}Rn source region [4.112].

High salinity groundwaters. It has been widely observed that highly saline waters, including formation waters associated with hydrocarbon deposits, are highly enriched in Ra (e.g. Kraemer [4.98], Dickson [4.113]). However, this may be due to limited removal of Ra rather than to increased supply of Ra. Average crustal rocks with 2.7 ppm U have activities of 3.4×10^5 Bq/kg. In an aquifer with e.g. 10% porosity and rock density of 2.8 g/cm^3, a litre of groundwater is associated with 25 kg of rock with 8.6×10^6 Bq/kg. Even if only $<10^{-4}$ of the ^{226}Ra produced in such an aquifer is continuously released by recoil, then it can support groundwater steady state Ra concentrations at the levels shown in Fig. 4.5. Therefore, there is generally no need for rocks with unusually high values of

^{238}U, or unusually high release rates, to explain such concentrations. Using ^{222}Rn concentrations as a measure of recoil supply, it has been shown that increased Ra concentrations in a suite of saline shallow groundwaters is due to lower adsorption rather than increased supply [4.114], though these samples had only 0.04–0.43 Bq/kg of ^{226}Ra (Fig. 4.5).

In some cases, Ra may be supplied by relatively small rock units, such as organic rich rocks strongly enriched in U. Further, Ra may be supplied not only by recoil but also by leaching, and continuous removal may result in substantial depletions of Ra in the rock. Ilani et al. [4.115] found that organic rich rocks in the vicinity of brines enriched in Ra near Galilee in Israel were also enriched in U, but substantially deficient in ^{226}Ra. This indicates that waters flowing past were continuously leaching Ra preferentially to U, which is insoluble under the reducing conditions of the sediment. A similar feature was found in rocks from western Israel, where brines entering a freshwater aquifer passing through organic rich deposits leached Ra and left rock with a low (^{226}Ra/^{238}U) ratio, and generated relatively fresh waters with high ^{226}Ra concentrations [4.116].

The behaviour of Ra in saline waters has generally been explained by sorption processes in secondary mineral phases (e.g. Zukin [4.117]) due to:

- Competition by other, more abundant cations for adsorption sites [4.113, 4.118], as demonstrated in laboratory experiments [4.119] of Ra on sandstone from groundwaters of different ionic strengths;
- Dissolution of Fe and Mn phases in anoxic brines, thereby decreasing the availability of adsorption sites [4.120];
- Increases in mineral surface charge [4.121] due to decreases in pH;
- Increases in stabilities of inorganic complexes such as chloride complexes [4.120, 4.122];
- Increased solubility of sulphate minerals [4.123] releasing recently incorporated Ra or limiting removal by precipitation;
- The presence of strong dissolved organic complexes [4.6, 4.124].

Where there are strong changes in groundwater salinity, e.g.by mixing, continuous changes in parameter values along flowlines can occur, and Ra evolutions are more complicated. Additionally, Ra may be deposited on aquifer surfaces and so may be a local source of ^{222}Rn [4.94]. For example, in the deep brines of the Palo Duro Basin, the saturation of barite and gypsum controls dissolved Ra concentrations [4.101]. Gonneea et al. [4.106] observed that adsorption decreased with increased salinity within an aquifer where saltwater intrusion occurs, although it was not possible to separate the effects of ion exchange from those due to Mn and Fe cycling due to redox changes.

Where Ra is supplied to waters that subsequently travel under conditions of minimal adsorption, the transit time to discharge points can be calculated. Kadko et al. [4.125] used Ra isotopes to determine transit times in a hydrothermal system in Iceland, where weathering of hot basalts at depth supplies Ra and generates waters with high total dissolved solids, low pH and high temperatures. During the subsequent ascent of these waters, Ra is neither lost by adsorption nor precipitation, nor does additional input occur, and the relative abundances of the Ra isotopes evolve only through decay according to their different half-lives. The Ra isotope composition of the discharged waters then provides a transit time of approximately 5 years. Similar calculations have been performed for Yellowstone hot spring waters [4.97].

4.3.1.3. Quantifying Ra adsorption and transport rates

Although various factors affecting the adsorption of Ra on aquifer rocks has been identified from relationships of groundwater Ra concentrations and aquifer characteristics, this information cannot generally be used to quantify Ra adsorption. As with most trace elements, the extent of adsorption can be determined from analyses of aquifer rocks or laboratory experiments, but it is difficult to obtain a bulk average value due to the heterogeneous distribution of secondary phases. Decay series systematics of nuclides in groundwater provide the potential for readily quantifying parameters of water–rock interaction from direct measurements of waters alone, with source terms and adsorption coefficients inferred from comparison between the different radionuclides. Sampling of large volumes or from a number of wells can obtain parameter values for larger volumes of aquifer. Once bulk adsorption partition coefficients are obtained, the rate of migration of Ra from point sources can be determined.

Groundwater models. Mathematical treatments of simple aquifer models have been extensively developed by various authors [4.126–4.131], and summarized in Refs [4.132, 4.133]. By modelling the processes of weathering, recoil, decay, adsorption and precipitation during advective transport in aquifers, these studies provide operational rates of transport and of water–rock interaction processes. These models are independent of the actual mechanisms involved, and so complement physical chemistry studies that can identify the controlling chemical processes. Most calculations that have been published elsewhere to constrain Ra behaviour can be derived from more fully developed mathematical treatments, although with simplifying assumptions that are not always explicitly stated or justified. These models have not been extended to non-steady-state conditions, such as in the vadose zone, except for U [4.134], in part because it is difficult to obtain sufficient quantities of vadose zone water to analyse short lived nuclides. In this case, inferences must be made from soil analyses [4.135].

The processes involving the ^{238}U decay series that affect ^{226}Ra, its direct parent ^{230}Th and daughter ^{222}Rn,are shown in Fig. 4.6, while those involving the ^{232}Th decay series that affect ^{228}Ra and ^{224}Ra, along with the parent Th isotopes are shown in Fig. 4.7 (from Ref. [4.133]). Although there is some data on ^{223}Ra, there have not been any extensive studies of the ^{235}U chain.

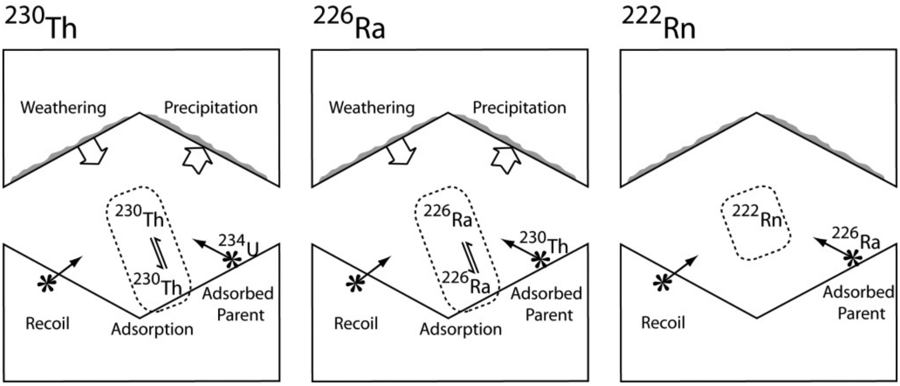

FIG. 4.6. The processes that affect concentrations of the combined dissolved and adsorbed inventories (surrounded by dotted lines) of ^{226}Ra, as well as parent ^{230}Th and daughter ^{222}Rn.

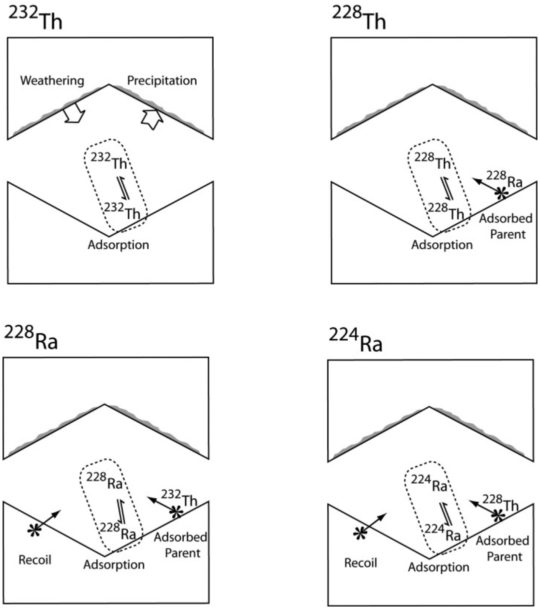

FIG. 4.7. The processes that affect concentrations of the combined dissolved and adsorbed inventories (surrounded by dotted lines) of ^{228}Ra and ^{228}Ra, as well as parent ^{232}Th and ^{228}Th.

Leaching of Ra from aquifer rocks is often referred to,although this is often an ill-defined process. Non-crystalline materials such as U bearing organic material may allow internal migration, and consequent loss, of poorly bound atoms such as Ra. Leaching of daughter radionuclides from damaged crystal sites is widely cited as an important process, but has not been experimentally demonstrated. While atoms implanted from outside the crystal lattice may be free to migrate back out through the damaged lattice, atoms produced within the mineral and not ejected across the mineral surface are unlikely to diffuse through the undamaged structure to the surface.

*The importance of weathering***.** The ratio of input by weathering to input by recoil for a nuclide *i* is:

$$\frac{\text{weathering rate } S_{weath}}{\text{recoil rate } S_{weath}} = \frac{w_i}{\varepsilon \lambda_i} \tag{4.5}$$

where w_i is the weathering rate constant for isotope *i*. Values of recoil fraction $\varepsilon \sim 10^{-2}$ have often been inferred from Rn data (see below). For ^{223}Ra, ^{224}Ra and ^{228}Ra, where $\lambda > 0.12$ a^{-1}, the rate of supply of these isotopes by weathering is less than recoil when $w_i < 10^{-3}$; that is, when less than 0.1% of the aquifer is weathered per year. This is certainly the case for most circumstances, and so the supply of these isotopes is predominately by recoil, and weathering can be neglected. For ^{226}Ra, with $\lambda_{226} = 4.33 \times 10^{-4}$/a, weathering inputs are only important if $w_{226} < 4 \times 10^{-6}$/a, or even less for lower recoil rates. Weathering rate constants that are lower [4.129, 4.136] and higher (see, e.g., Ref. [4.137]) have been reported for U series nuclides. Therefore, the weathering supply of ^{226}Ra will ideally be considered for each site.

The importance of precipitation. The ratio of removal by precipitation to removal by decay for a nuclide *i* is

$$\frac{\text{Precipitation rate}}{\text{Decay rate}} = \frac{Q_i}{\lambda_i K_i} \tag{4.6}$$

For ^{223}Ra, ^{224}Ra and ^{228}Ra, where $\lambda > 0.12$ a^{-1}, even for relatively low values for K the value of the precipitation rate constant Q will have to be unreasonably large for precipitation to be significant. However, for ^{226}Ra, with $\lambda_{226} = 4.33 \times 10^{-4}$ a^{-1}, precipitation will ideally be considered.

Evolving Ra concentrations. Water entering into an aquifer will start to accumulate Ra from weathering, recoil and decay of Th parent isotopes, until the isotope Ra concentrations reach a steady state level. This level can be most clearly understood by considering mobile Ra, that is, dissolved and adsorbed Ra together, as a single population defined as the dissolved concentration times $(1+K_D)$ $(\approx K_D)$ [4.133]. If the concentrations are in steady state, there is no longer a change in concentration along a flow line, and so there is no advection term. The inputs are then weathering, recoil and production from the decay of adsorbed and dissolved parent nuclides, while the only outputs are decay and precipitation. Dissolved radionuclides in water entering an aquifer, or where aquifer conditions are different, will have concentrations that evolve towards steady state concentrations exponentially over a characteristic distance $\bar{x}_i$ [4.130, 4.132]:

$$\bar{x}_i = \frac{v}{\lambda_i\left(K_i\right)+Q} \tag{4.7}$$

where v is the flow velocity. While the shorter-lived isotopes will generally adjust to local conditions over short distances, ^{226}Ra, with a much longer half-life, requires a much longer distance to achieve a constant concentration. The distance over which this occurs depends upon K, the groundwater flow rate v and the precipitation rate. Therefore, ^{226}Ra concentration gradients may be found over greater distances than those of the other Ra isotopes, resulting in substantial Ra isotope ratio variations. Such variations therefore can be used to identify nearby changes in aquifer conditions. For example, Martin and Akber [4.138] found that when increases in sulphate lead to Ra precipitation, the ratio of short lived Ra isotopes to ^{226}Ra was high due to their more rapid ingrowth.

Steady state Ra concentrations. At steady state, the removal rates (activity of dissolved and absorbed ^{226}Ra, and precipitation) are equal to inputs (^{226}Ra recoil rate and production from dissolved and absorbed ^{230}Th), so that [4.133]:

$$\left({}^{226}\mathrm{Ra}\right)_w = \frac{S_{\mathrm{Recoil}} + \left({}^{230}\mathrm{Th}\right)_w K_{\mathrm{Th}}}{K_{\mathrm{Ra}} + Q_{\mathrm{Ra}} / \lambda_{226}} \tag{4.8}$$

Variations in ^{226}Ra concentrations can clearly depend upon the distribution of ^{230}Th, as well as the recoil input rate.

For ^{228}Ra, weathering and precipitation can be neglected, and so at steady state removal (activity of dissolved and adsorbed ^{228}Ra) by decay is equal to inputs from recoil from ^{232}Th within the solids and from decay of adsorbed ^{232}Th [4.132]:

$$\left({}^{228}\mathrm{Ra}\right)_w K_{\mathrm{Ra}} = S_{\mathrm{Recoil}} = \left({}^{232}\mathrm{Th}\right)_w K_{\mathrm{Th}} \tag{4.9}$$

For ^{228}Th, weathering can also be neglected. ^{228}Ra decays by beta decay to the short lived ^{228}Ac, which rapidly decays to ^{228}Th. Since the decays of both ^{228}Ra and ^{228}Ac are low energy, there is no recoil of ^{228}Th from within minerals. Consequently, ^{228}Th outside aquifer minerals (largely adsorbed) is supplied only by largely adsorbed ^{228}Ra and is lost by decay [4.132]:

$$\left({}^{228}\mathrm{Th}\right)_w K_{\mathrm{Th}} = \left({}^{228}\mathrm{Ra}\right)_w K_{\mathrm{Ra}} \tag{4.10}$$

For ^{224}Ra, the amount in groundwater is largely supplied by recoil from ^{228}Th in the host rock minerals, as well as ^{228}Th on the mineral surfaces (which was in turn supplied by ^{228}Ra). Loss of ^{224}Ra is by decay. Therefore, in steady state [4.133]:

$$\left({}^{224}\mathrm{Ra}\right)_w K_{\mathrm{Ra}} = S_{\mathrm{Recoil}} + \left({}^{228}\mathrm{Ra}\right)\mathrm{Th}_w K_{\mathrm{Th}} \tag{4.11}$$

The above equations can be used to constrain the adsorption partition coefficient for Ra, as well as the adsorption partition coefficient of Th and the recoil rate of Ra.

(^{226}Ra/^{228}Ra) ratios and aquifer rock U/Th ratios. Since ^{228}Ra can provide a significant fraction of Ra activity in groundwater, understanding the controls on the (^{226}Ra/^{228}Ra) ratio is useful for predicting the total Ra activity from ^{226}Ra concentrations [4.89]. This ratio in groundwater is dependent upon the (^{238}U/^{232}Th) ratio of the host rock, and so provides information on the relative recoil rates from the two decay series. The equations above lead to [4.133]:

$$\frac{\left({}^{226}\mathrm{Ra}\right)_w}{\left({}^{228}\mathrm{Ra}\right)_w} = \left[\frac{{}^{230}\mathrm{U}}{{}^{232}\mathrm{Th}}\right]_{\mathrm{Rock}} \frac{{}^{\varepsilon}226}{{}^{\varepsilon}228} \tag{4.12}$$

If the amount of adsorbed Th is minor, and the recoil rates for the two chains are equal, then the (^{226}Ra/^{228}Ra) ratio is equal to the (^{238}U/^{232}Th) rock ratio. Measured values of (^{226}Ra/^{228}Ra) often cluster around the rock production ratio (e.g. Ref. [4.96]), suggesting that such conditions generally apply. Sturchio et al. [4.139] found a mean ratio of 3.3 in carbonate rocks, reflecting the low Th/U ratio of those rocks. In bedrock aquifer samples from Finland, samples had ^{226}Ra/^{228}Ra of 0.3 to 26 that generally correlated with concentrations of ^{226}Ra of <0.004 to 1.9 Bq/L [4.92]. This was attributed to variations in the Th/U ratio in the host rock, in a region where U redistribution has been substantial and has generated U mineralization. For comparison, the average upper crust has a (^{238}U/^{232}Th) activity ratio of ~0.8.

Significant deviations in (^{226}Ra/^{228}Ra)$_w$ from the aquifer rock (^{238}U/^{232}Th)$_w$ ratio do occur. Luo et al [4.129] found (^{226}Ra/^{228}Ra) ratios of 0.34–1.4 in a basaltic aquifer, compared to a bulk rock (^{238}U/^{232}Th) value of 0.9. Almeida et al. [4.110] reported mean concentrations in a ratio of 0.09 for groundwaters from Brazil, and King et al. [4.89] found values as low as 0.07 in crystalline rocks. Variations could be due to a number of reasons. Different distributions of U and Th, resulting in different recoil rates for the two Ra isotopes [4.135], may be due to weathering and adsorption of U, increasing the amount of ^{230}Th supplying ^{226}Ra, and so increasing the ratio, or to adsorption of a significant amount of ^{232}Th, supplying more ^{228}Ra [4.97].

There may also be non-steady-state conditions nearby where aquifer characteristics have changed. For example, a low mean ratio of 0.16 in saline waters from granites has been ascribed to low U/Th ratios in weathered surfaces of the aquifer [4.113], although accompanying high (^{223}Ra/^{226}Ra) ratios (see below) indicate that steady state concentrations have not been reached.

(^{223}Ra/^{226}Ra) ratio and steady state conditions. Since ^{235}U and ^{238}U are present in constant proportions everywhere and so are located in the same places, there are no fractionations between their decay series due to their siting in the host rock. ^{223}Ra and ^{226}Ra are both supplied through 3 α decays, as well as decay of adsorbed U, and have a highly surface reactive intermediate parent (^{231}Pa or ^{230}Th). Therefore, waters can be expected to have a ratio similar to the rock (^{235}U/^{238}U) activity ratio of 0.046. Where ^{226}Ra has not reached a steady state concentration in flowing groundwater after recharge or precipitation owing to its longer half-life, either lower or higher ratios may be found locally [4.127]. Martin and Akber [4.138] found (^{223}Ra/^{226}Ra)$_w$ ratios that were substantially above the rock value of 0.046 in samples that were saturated in barite. They suggested this was due to precipitation of both Ra isotopes, followed by a more rapid return to steady state concentrations of the shorter lived isotope immediately beyond sites of precipitation. Such data therefore could be used to identify when ^{226}Ra was precipitated. Brines from Western Australia had an average value of 0.3, also indicating changing conditions of Ra supply [4.113].

(^{224}Ra/^{228}Ra) ratios. As members of the same decay series, ^{224}Ra and ^{228}Ra isotopes are the most closely related. The activity of ^{228}Ra in groundwater is from recoil from ^{232}Th in minerals and decay of adsorbed ^{232}Th. This ^{228}Ra decays to ^{228}Th and then to ^{224}Ra, which is supplied by a second recoil term. The concentrations are related by the following equation [4.132]:

$$\left[\frac{^{224}\mathrm{Ra}}{^{224}\mathrm{Ra}}\right]_w = \frac{2S_{\mathrm{recoil}} + \left(^{232}\mathrm{Th}\right)_w K_{\mathrm{Th}}}{S_{\mathrm{recoil}} + \left(^{232}\mathrm{Th}\right)_w K_{\mathrm{Th}}} \tag{4.13}$$

The $(^{224}Ra/^{228}Ra)_w$ ratio ranges between 1, if production from adsorbed ^{232}Th is the dominant term, to 2, if the dominant supply is from recoil. This is a comparison between two small fractions of the total ^{232}Th present, the amount of adsorbed ^{232}Th that may release all its daughter ^{226}Ra to the fraction of ^{232}Th that is within recoil distance of the surface. Therefore, it cannot be easily constrained from analysis of aquifer materials. Krishnaswami et al. [4.126], assuming no adsorbed ^{232}Th, calculated a model ratio of 0.67 taking into account progressive depletion along the decay series at grain boundaries, and 1.2 if ^{228}Ra and ^{228}Th are adsorbed onto surfaces and continue to supply daughters into the groundwater by direct recoil. Reported values for fresh groundwaters generally fall in a narrow range of 0.5–2.2 [4.126, 4.129, 4.131]. Much higher values have also been reported (e.g. Refs [4.114, 4.127]). Ratios >2 require a different explanation. Along a flowline, ^{224}Ra will reach a constant concentration more rapidly than ^{228}Ra, and so higher values of $(^{224}Ra/^{228}Ra)$ may be observed in recently recharged waters [4.127, 4.130], or immediately downgradient of Ra precipitation [4.89].

Recoil rates and ^{222}Rn concentrations. Recoil rates can be most readily estimated from ^{222}Rn concentrations. Since Rn is an unreactive noble gas, the ^{222}Rn that has been released is entirely dissolved and so can be readily measured. Activities in groundwaters typically range between 3 and 30 × 10^4 Bq/L, though values up to 10^2 times higher have been reported [4.140]. Since it is only removed by decay, the activity is equal to the recoil supply rate from the decay of ^{226}Ra (Fig. 4.6). Adsorbed ^{226}Ra also supplies ^{222}Rn, although this is often neglected.

The fraction of ^{222}Rn atoms produced that are recoiled (ε) is dependent upon the fraction of ^{226}Ra that is within a recoil distance of ~20nm of mineral surfaces, and so on the size of the ^{226}Ra bearing grains, with small grains recoiling a larger fraction of ^{222}Rn. The exact value depends upon the geometry of the grains. Measured ^{222}Rn groundwater activities have been obtained that correspond to up to ~10% of the amount being produced in the aquifer rock [4.126]. The size of spherical grains required to produce such high emanation rates are several microns in diameter. This is generally below the typical size of primary U bearing minerals and so ^{226}Ra in surface coatings is often considered the main cause of high emanation fractions. These were created during the evolution of the source rocks through weathering, transport of sediment, or deposition. An interesting example is the very high emanation factors (up to 0.3) of terra rossa sediments formed from the insoluble residue of carbonate rocks, which have incorporated U onto near surface sites [4.141].

For U bearing minerals that contain all the nuclides in approximately secular equilibrium, recoil rates might be expected to be the same for all daughters produced by α decay. However, the recoil of daughter atoms from a mineral results in depletion near the surface of parent atoms for the next nuclide in the decay chain, although this depletion is partly counterbalanced by the recoil of atoms from further within the mineral towards the mineral surface. This effect advances progressively along each chain, but is not substantial; the recoil rate of ^{226}Ra is ~16% greater than ^{222}Rn [4.126].

The concentration of ^{222}Rn in groundwater can be related to recoil, as well as to production from Ra adsorbed and in solution, by considering the steady state concentrations of all the radionuclides along the ^{238}U decay series. Luo et al. [4.128] calculated values of 0.1–0.2 for a basaltic aquifer, so that recoil from mineral phases accounts for 10–20% of the dissolved ^{222}Rn. Although recoil coefficients are often taken directly from the ^{222}Rn concentrations, this demonstrates that a significant amount of the ^{222}Rn can be supplied by adsorbed ^{226}Ra.

Ra adsorption coefficients. A value for the Ra adsorption coefficient can be obtained from measurements of other radionuclides in the decay series, especially ^{222}Rn. This is simplest for ^{224}Ra, which is generally in steady state. Where it is largely supplied by recoil from within minerals rather than from decay of adsorbed species, and U and Th are similarly distributed, then the activity of adsorbed and dissolved ^{224}Ra of $K_{Ra}(^{224}\text{Ra})$ is equal to the activity of dissolved ^{222}Rn, so that $K_{\text{Ra}} = (^{222}\text{Rn}/^{224}\text{Ra})$ (see Refs [4.129, 4.132]).

Reported (^{222}Rn/^{224}Ra) ratios in fresh groundwaters of $(0.5–5) \times 10^4$ [4.126, 4.129, 4.131] notably do not exhibit a correlation with lithologies. The corresponding partition coefficients are 10^3–10^4. Higher (^{224}Ra/^{222}Rn) ratios found in saline groundwaters [4.114] are consistent with lower adsorption rates. A general measure of the extent of adsorption can also be obtained from (^{222}Rn/^{226}Ra) ratios (which is related to the (^{222}Rn/^{224}Ra) ratios by a factor of $(^{228}\text{Ra}/^{224}\text{Ra})(^{226}\text{Ra}/^{228}\text{Ra}) \sim 0.5$; (see Ref. [4.133]). For example, differences of 27 in mean values between aquifers have been interpreted as being due to differences in adsorption of Ra [4.89].

Note that the simple partition coefficients (K_i) are simply describing the present distribution of radionuclides in the aquifer. Nonetheless, when species concentrations are sufficiently small relative to the supporting electrolytes in solution and the capacity of the sorbing material, the distribution coefficients remain constant as concentrations change [4.142]. Extrapolation to much higher concentrations, for example due to anthropogenic contamination, requires further data on adsorption mechanisms and the relevant adsorption isotherms.

4.3.2. Surface Water

Physical processes. Radium released into surface water may be directly transferred in the water, or can deposit and migrate in bottom sediments. It can also be taken up by freshwater organisms, thus entering the food chain.

Radium transfer in surface water occurs through a combination of natural and anthropogenic processes, including the following [4.143, 4.144]:

- Diffusion and dispersion caused by gradients of concentration and the turbulent motion of water;
- Transport caused by water currents;
- Changes in the physicochemical form of Ra in surface water;
- Exchanges of contaminants between the dissolved and solid phases (suspended solids);
- Deposition and remobilization of the radionuclide following interaction with suspended matter and bottom sediments;
- Uptake by freshwater biota.

Hydraulic processes responsible for radionuclide transfer by water are mainly independent of radionuclide properties. Exchanges of radionuclides between the dissolved and solid phases as well as interaction with suspended matter and bottom sediments are strongly radionuclide specific, and quantification of Ra redistribution in the freshwater ecosystems requires evaluation of the physicochemical properties of radionuclides in water and sediments [4.12].

Diffusion and dispersion. The diffusion process assumes the movement of a radionuclide from areas of high concentrations to regions of low concentrations and the flux, F is related to the concentration gradient (Fick's first law);

$$F = -E\ grad(C) \tag{4.14}$$

where *grad* is the gradient of C and C is the radionuclide concentration in water. The values of the diffusion tensor components for molecular diffusion depend on the temperature and the mass of particles. Consequently, they depend on the specific features of the radionuclide. The order of magnitude of E in water ranges from 10^{-10} to 10^{-6} m^2/s [4.12].

Dispersion in the vertical direction is influenced by the stratification of water bodies. The vertical dispersion coefficient in a river can be assessed by the following approximate equation [4.136]:

$$E_z = \left(6.7\times10^{-2}\right)hu \approx \left(6.7\times10^{-3}\right)hU \tag{4.15}$$

where h is the water depth (m), $u*$ is the friction velocity (m/s) that is assumed to be 1/10 of U, the average flow velocity (m/s). Several empirical estimates of the vertical dispersion coefficient are available from the literature [4.145]. Horizontal transport in lake surface water is caused by currents and is also induced by the effect of wind [4.145].

The horizontal dispersion coefficient in lakes can be several orders of magnitude higher than E_z and can range from 10^{-3} to 10^{-2} m^2/s [4.146]. The values of the dispersion coefficients in rivers are strongly influenced by the water velocity. Turbulence effects imply that in a given river the dispersion coefficient increases with the water flux. An approximate estimate of E_x can be obtained by the following formula [4.147]:

$$E_x \approx \frac{0.11\,U\,L^2}{h} \tag{4.16}$$

where L is the width of the river.

There is no theoretical relationship for transverse diffusivity in rivers because this parameter is site specific. Nevertheless, for rivers with low meandering, it was suggested that E_y can be approximated by a semiempirical formula such as the one given in Ref. [4.148]:

$$E_y \approx 0.6\,h\,u^* \approx 6 \times 10^{-2}\,h\,U \tag{4.17}$$

Evaluations of longitudinal and transversal dispersion coefficients in rivers are available in the literature. Based on measurements performed in several North American rivers, Ref. [4.12] suggests values for the longitudinal (E_x) and the transverse (E_y) dispersion coefficients ranging from 7.6×10^{-1} to 1.5×10^3 m^2/s and from 4.8×10^{-3} to 1.1 m^2/s, respectively.

Transport by the current.

Whereas dispersion is due to the turbulent components of the water flow, advection (transport by the water current) is related to average water velocity v (m/s):

$$F = v \cdot C \tag{4.18}$$

The values for v in rivers normally range from a few decimeters per second to >1 m/s, depending on the river characteristics and the hydraulic regime [4.147].

Interaction between dissolved and solids phases of radionuclides

The interaction of radionuclides with bottom sediments and suspended particles is controlled by many environmental processes such as sedimentation and resuspension (Fig. 4.8). Seven ‘fast’ and ‘slow’ radionuclide fluxes within the system presented in Fig. 4.8 [4.147] can be aggregated as follows:

- — Radionuclide fluxes from dissolved form to particulate form and vice versa — rapid exchange processes (K_{wf}·C and K_{fw}·D_f);
- — Radionuclide fluxes from D_f to D_s and vice versa (K_{fs}·D_f and K_{sf}·D_s);
- — Radionuclide fluxes from water to Ds and vice versa (K_{ws}·C and K_{sw}·D_s);
- — Radionuclide irreversible burial in inactive sediments (K_s·D_s).

Assessment of the interaction of dissolved radionuclides with solid particles in suspension or deposited is usually based on the ‘K_d concept’, assuming a presence of an equilibration between the dissolved (C_w, Bq/m^3) and the adsorbed phases (C_s, Bq/kg) of a radionuclide:

$$K_d = \frac{C_s}{C_w} \tag{4.19}$$

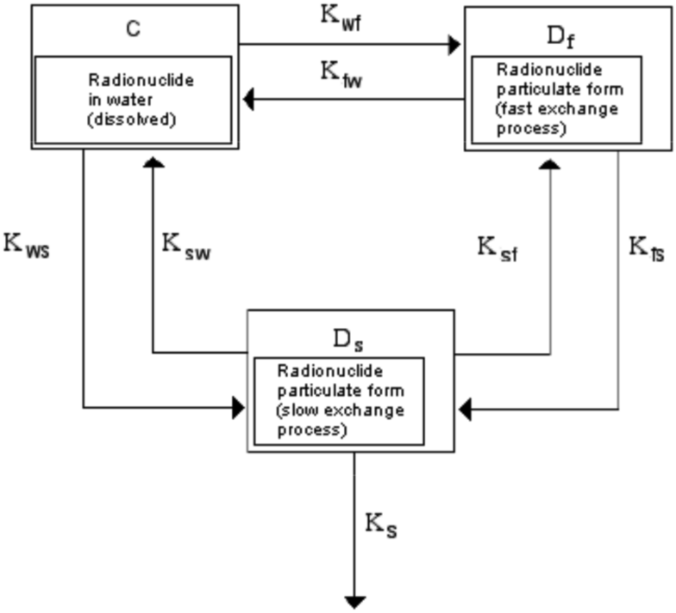

FIG. 4.8. Schematic structure of contaminant fluxes and environmental compartments involved in the processes of radionuclide migration to and from bottom sediment. The fast processes are marked in the subscript by the letter f and the slow processes by the letter s [4.145].

Based on an evaluation of 75 studies, Ref. [4.149] provides a geometric mean value for K_d of 7.4×10^3 with a geometric standard deviation around that mean of 3.1.

Although the kinetic parameters for the described redistribution of Ra in the system presented in Fig. 4.8 are not available in the literature, some assessments can be made based on relevant data given for other radionuclides with more or less similar properties such as ^{90}Sr [4.145].

4.3.3. Uptake by freshwater biota species

The uptake of Ra by freshwater species can take place in two ways [4.150]:

- Direct uptake from the water (and for fish, penetration of the element through the skin or gills during water filtration);
- Uptake from other media, such as bottom sediments for aquatic plants and some invertebrates, or food (ingestion, uptake of food and water, distribution through the digestive tract).

Although the contributions of those pathways to the total uptake of ^{226}Ra are not fully understood for any freshwater biota, many studies confirm the presence and importance of these pathways.

Models used for evaluation of the environmental impact of routine discharges on freshwater species normally assume that the aquatic organisms are in equilibrium with reference media such as water or sediments in their surrounding environment. The basic parameter used in such models is the concentration ratio (C_r) that relates radionuclide concentrations in biotic tissues to concentrations in the reference media [4.151]. The concentration ratio (also frequently known in aquatic research as the bioaccumulation factor) for aquatic species is defined as the ratio of the radionuclide concentration in certain biota species (C_b) from all exposure pathways to the radionuclide concentration in the water (C_w):

$$C_r = \frac{C_b}{C_w} \tag{4.20}$$

Concentration ratio values depend on a number of factors such as duration of exposure, age and metabolism rate; presence of other alkaline earth metals in the water, sediments or fish diet.

Freshwater biota species have different abilities to accumulate radionuclides and there are data from research documenting the influence of species differences on the C_r values [4.145]. As an example, the data of Table 4.5 show clear differences between the transfers of radionuclides to various fish species, displaying at the same time high variation in C_r values given for individual species.

Markose et al. [4.152] reported that increased calcium water levels reduced the uptake of ^{226}Ra by the freshwater gastropod *Viviparus bengalensis*. The experimental data for *Velesunio angasi* were consistent with ^{226}Ra accumulation, being inversely proportional to both calcium and magnesium water concentrations; for calcium the constant of proportionality, i.e. Ra = [Ca] is unity and for Mg it is about 0.1. These results indicate competitive inhibition of the uptake of ^{226}Ra by calcium, i.e. the mussel treated ^{226}Ra as a metabolic analogue of calcium [4.75]. Studies of the varying ^{228}Ra/^{226}Ra ratio in *Velesunio angasi* with mussel age have yielded an estimated biological half-life for Ra of approximately 9–13 years [4.153, 4.154].

Other examples illustrating the effect of the presence in the water of analogue elements such as Ba, Ca and Sr, as well as age effect, are described elsewhere [4.150].

TABLE 4.5. Ra-226 CONCENTRATION RATIO VALUES FOR VARIOUS FRESHWATER FISH SPECIES (BQ/KG FW TISSUE / BQ/L WATER)

Species	C_r
Anguilla anguilla Linn.	29–53
Carassius carassius Linn.	700
Coregonus lavaretus maraena Bloch	50
Cyprinus carpio Linn.	350–500
Esox lucius Linn.	19–200
Gobio gobio Linn.	32–127
Leuciscus cephalus Linn.	24–58
Noemacheilus barbulatus Linn.	78
Perca fluviatilis Linn.	12–650
Rutilus rutilus Linn.	37–600
Salmo trutta m. fario Linn.	37–430
Thymallus thymallus Linn.	2.3–64
Tinca tinca Linn.	250

The lower concentration ratio values were found in the species *Coregonus lavaretus maraena* Bloch, which lives in the water column and feeds mainly on plankton. A higher Ra uptake was observed in benthophages and phytophages, mainly in *Tinea Tinea* Linn., *Cyprinus carpio* L., *Rutilus rutilus* L. and *Carassius carassius* L. These differences are evidently due to, among other factors, way of life, type of food, rate of metabolism, growth and sexual maturity.

Two large scale reviews of available data on the accumulation of radionuclides by freshwater biota were recently performed within the framework of the IAEA EMRAS I and EMRAS II projects (Environmental Modelling for Radiation Safety; see http://www-ns.iaea.org/projects/emras/). The purpose of the first review was to compile available data on radionuclide transfer to edible freshwater biota (Table 4.6), while the intention of the second review was to provide bioaccumulation factors for dose assessments for non-human species (Table 4.7). Accordingly, the first set of data mainly included bioaccumulation factors for edible tissues and the second set included data for dose calculation on reference freshwater biota groups.

TABLE 4.6. RADIUM CONCENTRATION RATIO VALUES FOR EDIBLE FRESHWATER BIOTA (BQ/KG FW TISSUE / BQ/L WATER)

Group of species	*n*	GM/AM	GSD/SD	Min	Max
Primary producers[1]	8	2.8×10^3	4.1×10^0	6.40×10^2	1.1×10^4
Fish (muscles)	21	4.0×10^0	6.8×10^0	6.0×10^{-2}	1.5×10^2
Algae	4	3.9×10^3	3.7×10^0	6.4×10^2	1.1×10^4
Macrophytes (generic)	4	2.0×10^3	2.7×10^0	9.8×10^2	9.0×10^3
Invertebrates	5	1.0×10^2	3.0×10^1	1.8	1.8×10^3

[1] Primary producers include edible algae, floating leafed and emergent plant tissues.

TABLE 4.7. RADIUM CONCENTRATION RATIO VALUES FOR REFERENCE WILDLIFE GROUPS IN FRESHWATER ECOSYSTEMS (BQ/KG FW WHOLE ORGANISM / BQ/L WATER)

Group of species	*n*	AM	AMSD	GM	GMSD	Min	Max
Crustacean	5	2.7×10^{2}	4.4×10^{2}	1.4×10^{2}	3.1×10^{0}	—	—
Fish	277	1.7×10^{2}	5.0×10^{2}	5.5×10^{1}	4.5×10^{0}	1.4×10^{-1}	4.8×10^{3}
Benthic feeding	88	3.1×10^{2}	8.1×10^{2}	1.1×10^{2}	4.2×10^{0}	1.4×10^{1}	4.8×10^{3}
Piscivorous	68	1.1×10^{2}	2.1×10^{2}	5.1×10^{1}	3.5×10^{0}	6.7×10^{0}	8.5×10^{2}
Mammal herbivorous	45	2.1×10^{-1}	1.6×10^{-1}	1.7×10^{-1}	1.9×10^{0}	1.0×10^{-1}	5.0×10^{-1}
Mollusc — bivalve	43	2.4×10^{4}	3.5×10^{4}	1.4×10^{4}	2.9×10^{0}	1.2×10^{1}	1.3×10^{5}
Phytoplankton	40	5.5×10^{2}	7.3×10^{2}	3.3×10^{2}	2.7×10^{0}	1.8×10^{2}	2.4×10^{3}
Reptile	18	8.0×10^{2}	1.5×10^{3}	3.7×10^{2}	3.4×10^{0}	1.0×10^{2}	4.0×10^{3}
Vascular plant	73	2.2×10^{3}	2.7×10^{3}	1.4×10^{3}	2.6×10^{0}	4.0×10^{2}	1.0×10^{4}

— = no data available

The highest C_r values for edible freshwater biota were found to be in algae, floating leafed and emergent plant tissues, while the minimum values were found to be in flesh of fish.

In terms of whole body concentrations, the highest values were found to be in bivalve molluscs, due to high accumulation of Ra in the shell, in vascular plants and in reptiles.

The C_r values for fish muscles calculated based on whole body data with the aid of a whole body to tissue (muscles) conversion factor of 2.4 [4.155] range from 7.0×10^{-1} to 1.0×10^{2} (Bq/kg/Bq/L water, FW). This range is rather similar to that given in Table 4.6, and the geometric mean C_r values for the fish muscles derived based on such an approach from Table 4.7 are very similar to the corresponding value given for fish in Table 4.8.

4.4. MARINE ENVIRONMENT

The distribution of Ra in estuaries, coastal waters and the open ocean has been discussed in Section 3.5. Here we discuss the inputs of Ra isotopes to the ocean, and two applications that derive from these inputs. It must be noted that concentration units for Ra in seawater are generally expressed as dpm/100 kg. This unit was adopted by the Geochemical Ocean Section Study (GEOSECS) in 1970 [4.156] and for consistency has been used since. Fluxes of Ra are generally expressed as atoms/a.

4.4.1. Radium input to the ocean

Uranium is an abundant trace element in the ocean with a concentration averaging about 15 nM. However, Th produced from U decay is rapidly scavenged and transported to deep-sea sediments. Here, ^{230}Th decays to produce ^{226}Ra, which may be released from the particles holding the Th. Some of this Ra finds its way back to the ocean, where it mixes throughout the water column. This picture of U-Th-Ra behaviour was developed early in the study of marine radiation [4.157, 4.158].

The input of Ra to the ocean is a function of the Th content of sediments and rocks in contact with marine waters, of processes such as bioturbation and physical mixing that increase this contact, and of the half-life of the isotope of interest [4.159]. For ^{226}Ra, there are two major sources to the ocean. The classic source is the decay of ^{230}Th in deep-sea sediments [4.158, 4.160, 4.161]. This source is enhanced when organisms or physical processes mix the sediments and expose fresh surfaces to desorption. Another major source is submarine groundwater discharge (SGD) [4.162]. This source, which has only recently been appreciated, occurs when mixtures of seawater and fresh groundwater pass through permeable sediments and rocks on the continental margin. Hence, SGD enriches the upper ocean in ^{226}Ra. High concentrations of Ra in SGD occur because most SGD is not fresh water but a mixture of seawater and fresh groundwater. The high ionic strength decreases the Ra K_d and releases it into solution (see Section 4.4.2). Minor sources of ^{226}Ra include hydrothermal fluids, rivers, dust deposition and fine grained continental margin sediments. Because the mixing time of the ocean is on the order of the half-life of ^{226}Ra, this isotope is mixed throughout the ocean. In spite of the large SGD source, the upper ocean is depleted compared to the deep sea because some Ra is removed in the particle flux. Typical profiles of ^{226}Ra as a function of depth in different ocean basins are shown in Fig. 4.9 [4.163].

The highest concentrations occur in the deep north Pacific Ocean. This is in accord with the general pattern of ocean circulation that results in the oldest ocean waters being found in this region [4.164]. These old waters have accumulated Ra that has been remobilized from the particle flux.

Deep-sea inventories of ^{228}Ra are controlled by the decay of ^{232}Th in deep-sea sediments and processes that mix the sediments [4.165]. The inventory

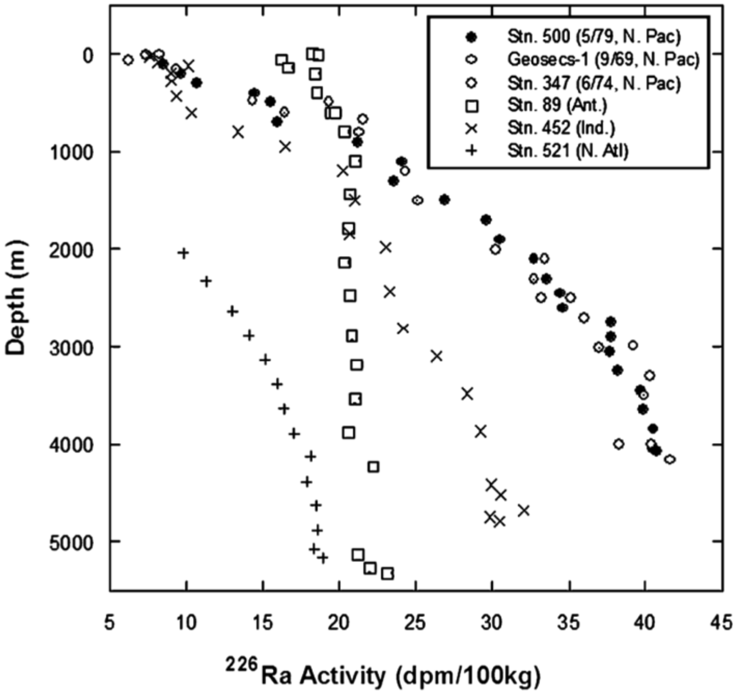

FIG. 4.9. The vertical distribution of ^{226}Ra in various ocean basins [4.163].

of ^{228}Ra in the upper ocean is supplied primarily by SGD, followed in decreasing importance by fine grained continental margin sediments, rivers and dust deposition [4.166]. Unlike ^{226}Ra, ^{228}Ra is not mixed throughout the ocean. Its short half-life restricts ^{228}Ra to approximately the upper and lower 1000 m of the water column. Activities are generally not measurable (<0.3 dpm per 100 kg) in the intermediate region.

In addition to the long lived isotopes, short lived ^{223}Ra and ^{224}Ra enter coastal waters from SGD, fine grained sediments and rivers. Because these isotopes are recoil products, their fluxes often exceed those of their parents. However, their short half-lives restrict their penetration into the ocean. The development of a technique to rapidly measure low activities of ^{223}Ra and ^{224}Ra in seawater [4.167] has driven an increased interest in studies of Ra in the ocean [4.168]. Concentrations of ^{223}Ra and ^{224}Ra as low as 5 atoms/L may be measured from samples with initial volumes of 200–1000 L [4.169]. This measurement technique is discussed in Section 2.5.

Studies of ^{223}Ra and ^{224}Ra have been used to estimate the mixing rate of near shore waters and the flushing times of estuaries, bays and lagoons [4.170–4.172].

Being able to quantify these rates allows workers to estimate fluxes of other components including nutrients, carbon, metals and ^{226}Ra and ^{228}Ra.

Much of the early work on the distribution of ^{226}Ra in the ocean was based on the mistaken assumption that the primary source was bottom sediments, accounting for over 90% of the input. Estimates made more recently suggest that inputs from SGD rival deep-sea inputs. The realization of the importance of SGD was first driven by measurements of strong enrichments in ^{226}Ra along coastlines not affected by river input [4.162]. Over the next 15 years, dozens of studies revealed strong coastal enrichments that could only be explained by SGD (see Refs [4.173–4.175] for summaries).

The SGD flux of ^{228}Ra to the Atlantic Ocean has been estimated to be 3.5×10^{23} atoms/a based on the flux required to maintain upper Atlantic inventories of ^{228}Ra [4.166]. Much less is known about the inventories of ^{228}Ra in other oceans, as only a few vertical profiles are available.

4.4.2. Sediment–radium interactions

Increasing the ionic strength of the water in contact with sediments reduces K_d and releases Ra into solution. Li et al. [4.176] concluded that desorption of Ra from suspended particles as they pass into salty estuarine water is the primary factor controlling the riverine input of Ra to the ocean. Webster et al. [4.177] modelled the effect of changing salinity on desorption of Ra from particles. They found that increasing the mean particle size of the sediment reduced both the exchangeable Ra concentration and the ratio of the exchange equilibrium constants of the sodium and Ra. They noted that only a portion of the total Ra associated with the sediments was in ion exchangeable form, the rest being retained within the mineral lattice. Rama and Moore [4.159] found that sediments containing abundant organic matter had lower K_ds than the same sediments after the organic matter had been removed by gentle oxidation.

4.4.3. Ra isotopes and coastal mixing and estuary flushing rates

Moore [4.171] measured Ra isotopes along several shore perpendicular transects off the coast of South Carolina, USA, and observed a linear decrease of ^{226}Ra and ^{228}Ra and an exponential decrease of ^{223}Ra and ^{224}Ra with distance from the coastline (Fig. 4.10). The linear decrease in the long lived isotopes indicated that conservative mixing between the enriched coastal source with the lower concentration open ocean waters controlled the concentrations over the wide continental shelf. The exponential decrease of the short lived isotopes indicated that radioactive decay was also a factor for these isotopes. These processes of mixing and decay may be described using a one dimensional eddy diffusion model with a mixing coefficient of 360–420 m^2/s [4.171]. The product of the mixing coefficient and the ^{226}Ra or ^{228}Ra gradient (Fig. 4.10) may be used to estimate the offshore fluxes of these isotopes.

This technique has now been refined and used in a number of studies [4.172, 4.178–4.184]. Knowledge of cross shelf mixing rates are important when calculating the input of dissolved terrestrial materials such as metals (especially Fe), dissolved organic and inorganic content, and nutrients to the ocean.

The short lived Ra isotopes may also be used to estimate the flushing times of estuaries, bays and coastal lagoons. These estimates usually rely on the change in activity ratio between a short and long lived isotope. Moore et al. [4.170]

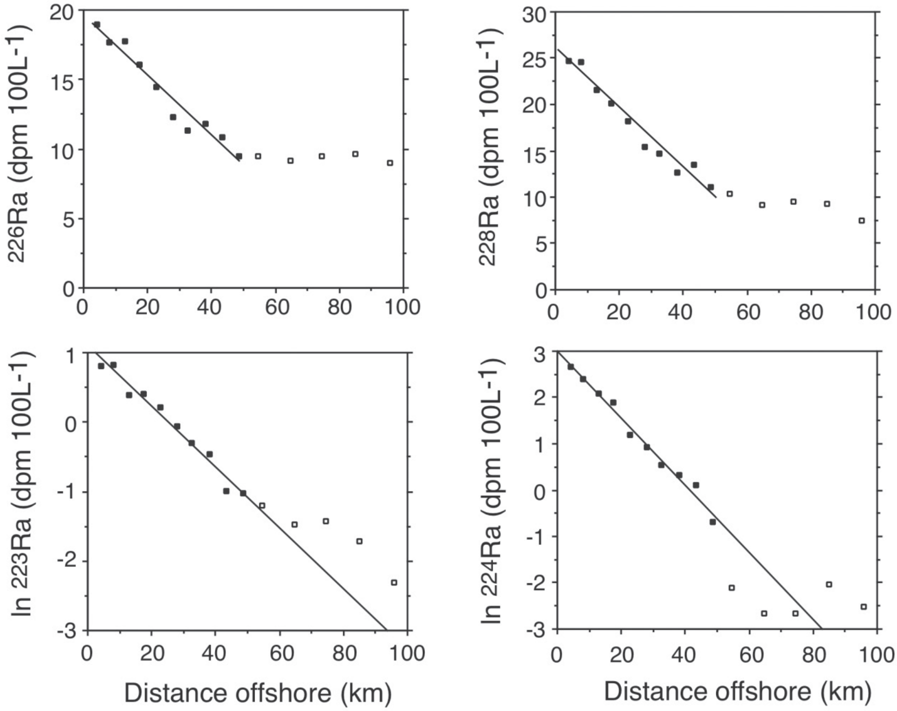

FIG. 4.10. The distributions of long lived (upper figures) and short lived (lower figures) Ra isotopes off the coast of South Carolina, USA. Note the linear decrease of ^{226}Ra and ^{228}Ra, indicating conservative mixing, and the exponential decreases of ^{223}Ra and ^{224}Ra, indicating mixing and radioactive decay. These measurements were made during a period of vertical stratification on the shelf, which confined inputs in the surface water to the coastal zone [4.171].

developed a model that utilized the difference in activity ratio between the flux of Ra to an estuary (in this case primarily SGD) and the inventory in the estuary:

$$T_f = \frac{\left({}^{224}\mathrm{Ra}\ /{}^{228}\mathrm{Ra}\right)_F - \left({}^{224}\mathrm{Ra}\ /{}^{228}\mathrm{Ra}\right)_I}{\left({}^{224}\mathrm{Ra}\ /{}^{228}\mathrm{Ra}\right)_I \lambda_{224}} \tag{4.21}$$

where T_f is the flushing time in days, $({}^{224}\mathrm{Ra}/{}^{228}\mathrm{Ra})_F$ is the activity ratio (of the flux to the water column and $({}^{224}\mathrm{Ra}/{}^{228}\mathrm{Ra})_I$ is the activity ratio of the dissolved inventory in the water column. The decay constant λ of ^{224}Ra is 0.19/day. This application has been used successfully in the Okatee estuary, SC, USA [4.170] and the Venice Lagoon, Italy [4.185].

4.4.4. Transfer to marine biota

The concentration ratio C_r (also known as the concentration factor), C_r = Bq/kg in biota × (Bq/kg in seawater), has been the parameter most used to quantitatively describe the accumulation of a given radionuclide in aquatic species relative to concentration in seawater. The IAEA has recommended [a compilation of C_r (CF) values for ^{226}Ra [4.186]. However, it will ideally be kept in mind that due to the relative scarcity of data they are mostly informed guesses and not entirely derived from field or laboratory data for several taxa. The current recommended C_r values may require revision in the near future to take into account newly published information on Ra in marine biota, particularly in fish.

There is no known biochemical function of Ra ions in cell metabolism, and therefore any accumulation of Ra in marine organisms could be due to chemical behaviour similar to other ions and would thus take place through fortuitious uptake. The consistency of Ra concentrations in specific groups of marine biota and the proportional relationship between Ra content in organisms and changes of Ra concentration in the environment further indicates that Ra uptake takes place in association with the uptake of some essential elements, such as calcium [4.187].

Uptake of ^{226}Ra from solution by freshwater algae was reported to be a linear response to ^{226}Ra concentration in the water and the same likely occurs with marine algae [4.188]. The possible transport of Ra^{2+} ions from seawater across cell membranes to inside the cell is considered likely to take place. There are three known basic membrane transport mechanisms, or ion pumps: Na^+–K^+, H^+–K^+ and Ca^{2+}.

Ra is an alkaline earth element and its chemical properties are partly similar to those of elements of the same group (Ca, Mg, Sr, Ba). The association of Ra to the metabolism of calcium is often made and there is a common belief that Ra ions follow Ca ions in the calcium metabolic pathways [4.187]. Therefore, the absorption of Ra^{2+} into the cells is likely to take place through the Ca^{2+} ion pumps [4.187]. However, whether Ra ions are truly absorbed into the intracellular medium or if they remain sorbed on the surface and outside the cell has not yet been experimentally verified [4.187, 4.188].

Early work showed that phytoplankton cells take up Ra (^{226}Ra) from dissolved Ra in seawater, and ^{226}Ra accumulation was investigated in comparison with accumulation of other alkaline earth elements [4.189]. Normalizing the concentrations C of element M to calcium content using a discrimination factor $DF_M = C_M/C_{Ca}$, it was shown that DF values for Ra relative to Ca fall into three groups. DF ranged from 20–60 for plankton, fish and algae; DF was below 10 and often between 0.1 to 4 for calcareous shells, and one DF value determined for siliceous diatoms was as high as 600. This suggested that diatoms accumulate Ra preferentially relative to calcium [4.189]. The analysis of mixed plankton samples from the Bahamas led to the observation that the DF of alkaline earth elements normalized on Ca showed indeed that Ra was selectively taken up by cells. Selectivity was as follows: Ra > Ba > Sr > Ca > Mg or 19 > 18 > 1.2 > 1.0 > 0.10, i.e. Ra and Ba were preferred, Sr was only slightly preferred relative to calcium and Mg was not accumulated preferentially compared to calcium. Furthermore, the DF values of plankton for alkaline earth elements relative to calcium were positively correlated with the ionic radii of elements, and their accumulation from seawater, including Ra, was suggested to take place by ion exchange [4.189].

Further work performed on ^{226}Ra in macrocellular algae in coastal areas of Porto Rico Island confirmed that at least three species of macroalgae concentrated Ra from seawater preferentially to calcium, although in other areas no discrimination between Ra and Ca was observed in the same algae species [4.190]. In the analysed macroalgae, calcium carbonate was deposited as aragonite, and Ra concentration did not correlate with the calcification degree of the algae. This was contrary to the common belief that ^{226}Ra could be used as a tracer for calcium, although this still seems true for systems where calcium is precipitated as apatite (calcium phosphate), such as in animal bone. It also found that Ra concentration follows the degree of calcification in the class Rhodophyta, though this was not observed in other algae classes. It was confirmed that the DF for Ra over Ca was true for most of the macroalgae, and often DF ranged between 2 and 40. It was also suggested that accumulation of ^{226}Ra in macroalgae could be due to two mechanisms: ion exchange or co-precipitation of Ra ions with the algae calcified matrix, and complex formation with the organic fraction of the algae [4.190].

Radium-226 in various algae is generally present in similar activity concentrations, but some algae seem to be highly selective to Ra and display high DF values relative to calcium. A high DF value of approximately 600 was reported in diatoms [4.189] . This was also noticed for Ba, the ionic radius of which is very close to that of Ra. It was hypothesized that microscopic diatoms that build their frustule with silicate significantly associate Ba to Si, and that the same may happen to some extent with Ra from seawater. Acantharians, planktonic organisms that build up their microscopic skeleton and cysts with strontium ($SrSO_4$), are also able to concentrate Ba and Ra from seawater. Planktonic Foraminifera, such as the common *Globigerina spp*., build their exoskeleton from calcium carbonate (calcite) and incorporate Ba, and thus are likely to also incorporate Ra [4.191–4.194]. Radium incorporation in aragonitic structures of calcified biologic structures, such as the otoliths of fish, has been used for the determination of age and growth rate of some marine species [4.195].

Experimental studies performed on Ba and Sr uptake by fish under laboratory conditions demonstrated that fish accumulate these alkaline earth elements proportionally to their concentration in the environment. The *DF* of Ba and Sr relative to Ca were shown to be affected by temperature and are useful as thermometers in current and paleoclimatic chemistry [4.192]. The same effect of temperature is likely to be verified with Ra and Ra/Ca *DF*, although no reports could be found in the published literature.

Diatoms, acantharians and foraminifera are supposed to play a key role in the Ba cycle in the oceans, including the formation of barite deposits on the sea floor that are also rich in Ra [4.196]. Phytoplankton and seaweed might thus play a central role in the biogeochemical cycling of Ra in the ocean and in particular in the removal of ^{226}Ra from the upper layer of the ocean.

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Chapter 5

DOSE ASSESSMENT

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5.1. MODELS AND DATA FOR ESTIMATING INTERNAL EXPOSURES TO HUMANS

Dosimetric models to estimate human internal exposures subsequent to incorporation of radionuclides via ingestion and inhalation have been developed by the ICRP; the most recent models for Ra isotopes are described in Ref. [5.1] for ingestion and in Ref. [5.2] for inhalation. The endpoints of those models are dose coefficients for ingestion and inhalation, which are calculated for six age groups (3 months, 1, 5, 10, 15 year old children and adults).

The dose coefficients are based on the equivalent dose rates received up to 70 years of age, following an acute intake, i.e. for a one year old child the dose contributions are integrated over a period of 69 years whereas for adults, the dose is integrated over a period of 50 years.

The key processes in the biokinetic models are adsorption of the radionuclides in the blood as well as distribution and retention in the organism. From these quantities, the time-integrated concentrations in the organs and tissues and the number of disintegrations during the integration period are calculated. For a specific organ, the integrated absorbed dose is calculated from:

- The number of decays during the integration period;
- The energy per decay;
- The energy deposited in a specific organ from radionuclides within this organ; and
- The energy deposited in a specific organ from radionuclides decaying in other organs and tissues.

Since the decay products of Ra isotopes are radioactive, the contributions of the daughter nuclides to the dose are taken into account considering the element dependent patterns for distribution and retention.

The model parameters applied in these biokinetic models are derived from all available and appropriate experiments and observations related to the uptake and distribution of radionuclides. Many of them were determined from animal studies.

Following ingestion, in the ICRP model, the transfer of Ra from the gut to the blood (resorption) is age dependent. The highest resorption is applied for infants, with 60%, while for adults 20% are applied and 30% for all other age groups.

The distribution and retention of Ra is described by a complex model simulation of the fluxes of Ra between different organs and tissues. Radium accumulates in the skeleton. The most important process for the long term retention is therefore the exchange of Ra between the skeleton and the other organs and tissues. For adults, the long term loss from the skeleton is equivalent to a biological half-life of the order of 10 years. More details on biokinetic modelling of Ra in humans are given in ICRP 67 [5.1].

For inhalation, the transfer from the blood depends on the age and the chemical form of Ra. In general, the ICRP takes into account three absorption classes indicated as S, M and F, which represent slow, medium and fast retention, respectively.

In Tables 5.1 and 5.2, the dose coefficients for ^{226}Ra and ^{228}Ra are summarized for ingestion and inhalation, respectively. In Ref. [5.1], the dose coefficients are given for more than 20 organs. In the tables, only the dose coefficients for effective dose and for the organs with the highest dose coefficients are given. For ingestion of ^{226}Ra and ^{228}Ra, the organs with the highest dose coefficients are bone surface, red bone marrow and liver. For inhalation, the dose coefficients for the lung and the extrathoracic airways are also important. As reported in ICRP 72 [5.2], there are large differences between the dose coefficients for the different absorption classes; however, in Ref. [5.2], class M is recommended for all compounds; therefore, only the values for this absorption class are given.

TABLE 5.1. DOSE COEFFICIENTS FOR INGESTION OF ^{226}Ra AND ^{228}Ra (SV/BQ)

Radio-nuclide	Organ/tissue	Age group (a) Dose coefficient					
		<1	1–2	2–7	7–12	12–17	>17
	f_1 value	0.6	0.3	0.3	0.3	0.3	0.2
^{226}Ra	Bone surface	1.6×10^{-4}	2.9×10^{-5}	2.3×10^{-5}	3.9×10^{-5}	9.4×10^{-5}	1.2×10^{-5}
	Liver	3.8×10^{-6}	1.5×10^{-6}	7.8×10^{-7}	5.3×10^{-7}	4.0×10^{-7}	1.8×10^{-7}
	Red bone marrow	2.0×10^{-5}	3.0×10^{-6}	1.8×10^{-6}	2.4×10^{-6}	4.1×10^{-6}	8.7×10^{-7}

TABLE 5.1. DOSE COEFFICIENTS FOR INGESTION OF ^{226}Ra AND ^{228}Ra (SV/BQ) (cont.)

Radionuclide	Organ/tissue	Age group (a) Dose coefficient					
		<1	1–2	2–7	7–12	12–17	>17
	Effective dose	4.7×10^{-6}	9.6×10^{-7}	6.2×10^{-7}	8.0×10^{-7}	1.5×10^{-6}	2.8×10^{-7}
^{228}Ra	Bone surface	8.5×10^{-4}	1.6×10^{-4}	1.1×10^{-4}	1.4×10^{-4}	2.3×10^{-4}	2.2×10^{-5}
	Liver	4.3×10^{-6}	9.6×10^{-6}	5.3×10^{-6}	4.7×10^{-6}	5.4×10^{-6}	1.0×10^{-6}
	Red bone marrow	1.3×10^{-4}	2.1×10^{-5}	1.2×10^{-5}	1.3×10^{-5}	1.8×10^{-5}	2.3×10^{-6}
	Effective dose	3.0×10^{-5}	5.7×10^{-6}	3.4×10^{-6}	3.9×10^{-6}	5.3×10^{-6}	6.9×10^{-7}

TABLE 5.2. DOSE COEFFICIENTS FOR INHALATION OF ^{226}Ra AND ^{228}Ra (SV/BQ)

Radionuclide	Organ/tissue	Age group (a) Dose coefficient					
		<1	1–2	2–7	7–12	12–17	>17
^{226}Ra	f_1-value	0.2	0.1	0.1	0.1	0.1	0.1
	Endotracheal airways	4.9×10^{-5}	3.8×10^{-5}	1.6×10^{-5}	1.1×10^{-5}	6.1×10^{-6}	6.0×10^{-6}
	Lung	1.2×10^{-4}	9.1×10^{-5}	5.7×10^{-5}	3.8×10^{-5}	3.3×10^{-5}	2.8×10^{-5}
	Bone surface	3.3×10^{-5}	1.1×10^{-5}	8.5×10^{-6}	1.5×10^{-5}	3.5×10^{-5}	7.4×10^{-6}
	Liver	8.4×10^{-7}	5.6×10^{-7}	2.8×10^{-7}	1.9×10^{-7}	1.5×10^{-7}	1.1×10^{-7}
	Red bone marrow	3.9×10^{-6}	1.1×10^{-6}	6.7×10^{-7}	9.1×10^{-7}	1.5×10^{-6}	5.2×10^{-7}
	Effective dose	1.5×10^{-5}	1.1×10^{-5}	7.0×10^{-6}	4.9×10^{-6}	4.5×10^{-6}	3.5×10^{-6}

TABLE 5.2. DOSE COEFFICIENTS FOR INHALATION OF ^{226}Ra AND ^{228}Ra (SV/BQ) (cont.)

Radio-nuclide	Organ/tissue	Age group (a) Dose coefficient					
		<1	1–2	2–7	7–12	12–17	>17
^{228}Ra	ET airways	3.1×10^{-5}	2.5×10^{-5}	1.2×10^{-5}	7.9×10^{-6}	4.6×10^{-6}	4.4×10^{-6}
	Lung	4.2×10^{-5}	3.6×10^{-5}	2.2×10^{-5}	1.4×10^{-5}	1.2×10^{-5}	9.7×10^{-6}
	Bone surface	2.7×10^{-4}	1.6×10^{-4}	1.2×10^{-4}	1.1×10^{-4}	1.3×10^{-4}	5.6×10^{-5}
	Liver	1.5×10^{-5}	9.2×10^{-6}	5.3×10^{-6}	3.6×10^{-6}	3.4×10^{-6}	2.4×10^{-6}
	Red bone marrow	4.2×10^{-5}	2.4×10^{-5}	1.4×10^{-5}	1.0×10^{-5}	1.0×10^{-5}	4.7×10^{-6}
	Effective dose	1.5×10^{-5}	1.0×10^{-5}	6.3×10^{-6}	4.6×10^{-6}	4.4×10^{-6}	2.6×10^{-6}

5.2. DOSE CONVERSION FACTORS FOR ESTIMATING EXTERNAL AND INTERNAL DOSES TO BIOTA

Plants and animals may be exposed to ionizing radiation from radionuclides in the environment by both external and internal exposure. Radionuclides distributed in the environment lead to external radiation exposure of the organisms living in or close to a contaminated medium. External exposures of biota are the result of complex and non-linear interactions of various factors:

- The contamination levels in the environment;
- The radionuclide specific decay properties characterized by the radiation type, the energies emitted and the yield;
- The geometrical relationship between the source of the radiation and the target organisms;
- The composition and shielding properties of materials/media in the environment;
- The habitat and size of the organism.

For the estimation of exposures to biota, models have been developed to derive dose conversion coefficients (DCCs) for a set of biota. Since it is impossible to consider all species of flora and fauna explicitly in dose assessments, DCCs are provided for a set of reference organisms that were selected within the FASSET and ERICA project to represent typical members of common ecosystems (e.g. Refs [5.3–5.5]). The reference organisms considered in this compilation are summarized in Table 5.3 [5.3–5.5]. For the calculation of DCCs for internal and external exposures, the following simplifying assumptions were made:

- The radionuclides are uniformly distributed within the body;
- The shape of all organisms is approximated by spheres and ellipsoids.

5.2.1. Internal exposure

The exposure due to radionuclides incorporated into the organism is determined by the activity concentration in the organism, the size of the organism and the type and the energy of the emitted radiation.

A key quantity for estimating internal doses is an absorbed fraction φ, which is defined as the fraction of energy emitted by a radiation source that is absorbed within the target tissue, organ or organism. In the simplest case, the organism is assumed to be in an infinite homogeneous medium and has uniformly distributed activity throughout its body. The densities of the medium and the organism's body are the same. Under these conditions, both internal (D_{int}) and external (D_{ext}) dose conversion coefficients (defined as absorbed dose rate per activity concentration in organism or medium) for monoenergetic radiation can be expressed as a function of the absorbed fraction [5.6–5.8]:

$$D_{\text{int}} = E \times \phi(E) \tag{5.1}$$

$$D_{\text{ext}} = E \times \left(1 - \phi(E)\right) \tag{5.2}$$

where E is the energy of a mono-energetic source. Equation 33 is an approximation that, in a strict sense, only holds if the organism and the surrounding medium are of the same density and elemental composition.

Absorbed fractions for photon and electron sources uniformly distributed in soft tissue spheres and ellipsoids immersed in an infinite water medium have been systematically calculated by Monte Carlo simulation for an energy range of 10 keV to 5 MeV, and a mass range from 10^{-6} to 10^{3} kg. This approach was also applied for calculation of the absorbed fractions for non-aquatic animals and their internal exposures. By means of rescaling and interpolation techniques [5.8] of the internal dose from this data set, conversion coefficients have been calculated for all reference organisms [5.9].

Dose conversion coefficients for external exposure were calculated separately for aquatic and terrestrial reference animals and plants. For aquatic organisms, which are immersed in water, external exposure is calculated according to Eqs (5.1) and (5.2).

TABLE 5.3. REFERENCE ORGANISMS DEFINED IN FASSET/ERICA AND REFERENCE ANIMALS AND PLANTS AS DEFINED BY ICRP

ERICA reference organisms (example)	ICRP reference animals and plants	Habitat	Mass (kg)
Terrestrial environment			
Detritivorous invertebrate (woodlouse)	—	On and in soil	1.7×10^{-4}
Insect	Bee	In air	5.9×10^{-4}
Lichen & bryophytes (bryophyte)	—	On soil	1.1×10^{-4}
Gastropod (snail)	—	On soil	1.4×10^{-3}
Grasses & herbs	Wild grass	On soil	2.6×10^{-3}
Soil invertebrate (earthworm)	Earthworm	In soil	5.2×10^{-3}
Amphibian (frog)	Frog		3.1×10^{-2}
Bird egg	Duck egg	On soil	5.0×10^{-2}
Burrowing mammal (rat)	Rat	In soil	3.1×10^{-1}
Reptile (snake)	—	On soil	7.4×10^{-1}
Wading bird (duck)	Duck	On soil	1.3×10^{0}
Large mammal (deer)	Deer	On soil	2.5×10^{2}
Tree	Pine tree	On soil	4.7×10^{2}
Shrub	—	On soil	—
Marine environment			
Phytoplankton		In water	6.5×10^{-11}
Zooplankton		In water	6.1×10^{-5}
Sea anemones / true corals		In water	1.8×10^{-3}

TABLE 5.3. REFERENCE ORGANISMS DEFINED IN FASSET/ERICA AND REFERENCE ANIMALS AND PLANTS AS DEFINED BY ICRP (cont.)

ERICA reference organisms (example)	ICRP reference animals and plants	Habitat	Mass (kg)
Macroalgae	Brown seaweed	In water	6.5×10^{-3}
Benthic mollusc		In water	1.6×10^{-2}
Polychaete worm		In water	1.7×10^{-2}
Vascular plant		In water	2.6×10^{-2}
Pelagic fish		In water	5.7×10^{-1}
Crustacean	Crab	In water	7.5×10^{-1}
Benthic fish	Flat fish	In water	1.3×10^{0}
Reptile (marine turtle)		In water	1.4×10^{2}
Mammal		In water	1.8×10^{2}
Sea anemones / true corals		In water	2.0×10^{2}
(Wading) bird	Duck	In water	1.3×10^{0}
Freshwater environment			
Phytoplankton		In water	2.1×10^{-12}
Zooplankton		In water	2.4×10^{-6}
Crustacean		In water	1.6×10^{-5}
Insect larvae		In water	1.8×10^{-5}
Vascular plant		In water	1.1×10^{-3}
Gastropod		In water	3.5×10^{-3}
Bivalve mollusc		In water	7.1×10^{-2}
Pelagic fish	Salmonid/trout	In water	1.3×10^{0}
Benthic fish		In water	1.5×10^{0}
Mammal		In water	3.9×10^{0}
Bird	Duck	In water	1.3×10^{0}
Amphibian	Frog	In water	3.1×10^{-2}

— = no data available

5.2.2. External exposure

For terrestrial reference animals and plants, the estimation of external exposures is more complex, since soil, air and organic matter differ considerably in composition and density. Therefore, the derivation of DCCs is based on radiation transport simulated for monoenergetic photons by means of Monte Carlo techniques [5.10]. Due to the complexity of the processes and the variability of life forms, reference geometries as defined by energy, contaminated media and organism sizes were considered in detail. External exposures under conditions for which specific calculations have not been made can then be estimated with sufficient accuracy by the application of interpolation techniques.

The dose conversion coefficients for ^{226}Ra and ^{228}Ra are summarized in Tables 47, 48 and 49 for terrestrial, marine and freshwater organisms, respectively.

The values for internal exposure are given in quantities of dose rate per unit activity concentration in the organisms (µGy/h per Bq/kg). The values are given for absorbed dose; i.e. radiation weighting factors to account for the effectiveness of the different radiation types in causing effects to biota are not applied, since the discussion on this topic is on going. To enable the estimation of the possible impact of the weighting factors of different kinds of radiation, the contributions of α radiation, low β radiation ($E \leq 10$ keV), β radiation ($E > 10$ keV) and γ radiation to the DCCs are provided.

Values for external exposures for aquatic organisms are given for a total immersion in water in units of µGy/h per Bq/L. For terrestrial organisms, various different source geometries are considered depending on the habitat of the organism concerned:

- For on or above soil organisms, two geometries are considered:
  - A planar source, the source being at a depth of 0.3 cm to account for surface roughness (µGy/h per Bq/m^2);
  - A 10 cm thick volume source (soil density: 1.6 g/cm^3) (µGy/h per Bq/kg);
- For in soil organisms, the values are given for organisms living in the middle of a volume source with a thickness of 50 cm (soil density: 1.6 g/cm^3) (µGy/h per Bq/kg).

Radioactive daughter nuclides are included in the calculation of the DCCs if their half-lives are shorter than 10 days.

TABLE 5.4. DOSE CONVERSION COEFFICIENTS FOR TERRESTRIAL REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE

Nuclide	Reference organism	Internal exposure				External exposure DCC for habitat/source:		
		DCC (µGyh^{1}·Bq^{1}·kg)	f_1 (%)	f_2 (%)	f_3 (%)	In soil/infinite (µGyh^{-1}·Bq^{-1}·kg)	On soil/planar (µGyh^{-1}·Bq^{-1}·m^{2})	On soil/volume (µGyh^{-1}·Bq^{-1}·kg)
^{226}Ra	Woodlouse	1.4×10^{-2}	97	0	3	9.1×10^{-4}	5.6×10^{-6}	3.5×10^{-4}
	Terrestrial insect (bee)	1.4×10^{-2}	97	0	3	—	5.6×10^{-6}	3.5×10^{-4}
	Terrestrial lichen (lichens and bryophytes)	1.4×10^{-2}	98	0	2	—	2.9×10^{-6}	1.8×10^{-4}
	Terrestrial gastropod (snail)	1.4×10^{-2}	97	0	3	9.1×10^{-4}	5.6×10^{-6}	3.5×10^{-4}
	Terrestrial grass (wild grass)	1.4×10^{-2}	97	0	3	—	1.3×10^{-5}	3.3×10^{-4}
	Earthworm (soil invertebrate)	1.4×10^{-2}	97	0	3	9.0×10^{-4}		
	Terrestrial amphibian (frog)	1.4×10^{-2}	96	0	4	8.9×10^{-4}	5.6×10^{-6}	3.4×10^{-4}
	Bird egg (duck egg)	1.4×10^{-2}	96	0	4	—	5.6×10^{-6}	3.4×10^{-4}
	Terrestrial burrowing mammal (rat)	1.4×10^{-2}	96	0	4	8.5×10^{-4}	5.5×10^{-6}	3.4×10^{-4}
	Terrestrial reptile (snake)	1.4×10^{-2}	96	0	4	8.2×10^{-4}	5.3×10^{-6}	3.3×10^{-4}
	Large terrestrial mammal (deer)	1.5×10^{-2}	92	0	8	—	2.8×10^{-6}	1.8×10^{-4}
	Tree (pine tree)	1.5×10^{-2}	93	0	7	—	3.9×10^{-6}	2.7×10^{-4}
	Terrestrial shrub	—	—	—	—	—	6.1×10^{-6}	3.2×10^{-4}
	Terrestrial wading bird (duck)	1.4×10^{-2}	—	—	—	—	5.2×10^{-6}* 4.5×10^{-6}**	3.2×10^{-4}* 3.0×10^{-4}**
^{228}Ra***	Woodlouse	2.2×10^{-4}	0	4	96	5.0×10^{-4}	3.2×10^{-6}	1.9×10^{-4}
	Terrestrial insect (bee)	2.5×10^{-4}	0	4	96	—	3.2×10^{-6}	1.9×10^{-4}
	Terrestrial lichen (lichens and bryophytes)	2.0×10^{-4}	0	5	95	—	1.7×10^{-6}	1.0×10^{-4}

TABLE 5.4. DOSE CONVERSION COEFFICIENTS FOR TERRESTRIAL REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE (cont).

Nuclide	Reference organism	Internal exposure				External exposure DCC for habitat/source:		
		DCC (μGyh^{1}·Bq^{1}·kg)	f_1 (%)	f_2 (%)	f_3 (%)	In soil/infinite (μGyh^{-1}·Bq^{-1}·kg)	On soil/planar (μGyh^{-1}·Bq^{-1}·m^{2})	On soil/volume (μGyh^{-1}·Bq^{-1}·kg)
	Terrestrial gastropod (snail)	2.6×10^{-4}	0	4	96	5.0×10^{-4}	3.2×10^{-6}	1.9×10^{-4}
	Terrestrial grass (wild grass)	2.6×10^{-4}	0	3	97	—	8.6×10^{-6}	1.9×10^{-4}
	Earthworm (soil invertebrate)	2.7×10^{-4}	0	3	97	5.0×10^{-4}		
	Terrestrial amphibian (frog)	3.0×10^{-4}	0	3	97	4.9×10^{-4}	3.2×10^{-6}	1.9×10^{-4}
	Bird egg (duck egg)	3.0×10^{-4}	0	3	97	—	3.1×10^{-6}	1.9×10^{-4}
	Terrestrial burrowing mammal (rat)	3.3×10^{-4}	0	3	97	4.7×10^{-4}	3.1×10^{-6}	1.9×10^{-4}
	Terrestrial reptile (snake)	3.2×10^{-4}	0	3	97	4.5×10^{-4}	3.0×10^{-6}	1.8×10^{-4}
	Large terrestrial mammal (deer)	6.1×10^{-4}	0	1	99	—	1.6×10^{-6}	9.7×10^{-5}
	Tree (pine tree)	5.7×10^{-4}	0	2	98	—	2.2×10^{-6}	1.5×10^{-4}
	Terrestrial shrub	—	—	—	—	—	3.6×10^{-6}	1.8×10^{-4}
	Terrestrial wading bird (duck)	3.6×10^{-4}					2.9×10^{-6} *	1.8×10^{-4} *
							2.5×10^{-6} **	1.7×10^{-4} **

* Height above ground (m) = 0

** Height above ground (m) = 3

*** The dose conversion coefficients for ^{228}Ra include the contributions of the daughter nuclide ^{228}Ac (half-life: 6.15 h).

— = no data available

TABLE 5.5. DOSE CONVERSION COEFFICIENTS FOR MARINE REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE

Nuclide	Reference organism	Internal exposure				External exposure
		DCC (μGy·h^{-1}·Bq^{-1}·kg)	f_1 (%)	f_2 (%)	f_3 (%)	DCC (μGyh^{-1}·Bq^{-1}·L)
^{226}Ra	Marine phytoplankton	9.1×10^{-7}	99	0	1	1.5×10^{-2}
	Zooplankton	1.4×10^{-2}	98	0	2	1.2×10^{-3}
	Sea anemone / true corals	1.4×10^{-2}	97	0	3	1.1×10^{-3}
	Macro algae (brown seaweed *)	1.4×10^{-2}	97	0	3	1.1×10^{-3}
	Benthic mollusc	1.4×10^{-2}	96	0	4	1.0×10^{-3}
	Vascular plant	1.4×10^{-2}	96	0	4	1.0×10^{-3}
	Marine worm (polychaete worm)	1.4×10^{-2}	96	0	4	1.1×10^{-3}
	Marine pelagic fish	1.4×10^{-2}	96	0	4	9.4×10^{-4}
	Marine crustacean (crab)	1.4×10^{-2}	96	0	4	9.2×10^{-4}
	Marine benthic fish (flatfish)	1.4×10^{-2}	96	0	4	9.7×10^{-4}
	Marine reptile	1.5×10^{-2}	93	0	7	5.1×10^{-4}
	Marine mammal (dolphin)	1.5×10^{-2}	93	0	7	5.0×10^{-4}
^{228}Ra	Marine phytoplankton	7.2×10^{-9}	0	8	92	8.4×10^{-4}
	Zooplankton	2.0×10^{-4}	0	5	95	6.4×10^{-4}

TABLE 5.5. DOSE CONVERSION COEFFICIENTS FOR MARINE REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE (cont.)

Nuclide	Reference organism	Internal exposure				External exposure
		DCC (μGy·h^{-1}·Bq^{-1}·kg)	f_1 (%)	f_2 (%)	f_3 (%)	DCC (μGyh^{-1}·Bq^{-1}·L)
	Sea anemone / true corals	2.6×10^{-4}	0	3	97	5.8×10^{-4}
	Macro algae (brown seaweed)	2.4×10^{-4}	0	4	96	6.0×10^{-4}
	Benthic mollusc	2.9×10^{-4}	0	3	97	5.6×10^{-4}
	Vascular plant	2.9×10^{-4}	0	3	97	5.5×10^{-4}
	Marine worm (polychaete worm)	2.7×10^{-4}	0	3	97	5.7×10^{-4}
	Marine pelagic fish	3.4×10^{-4}	0	3	97	5.1×10^{-4}
	Marine crustacean (crab)	3.5×10^{-4}	0	3	97	5.0×10^{-4}
	Marine benthic fish (flatfish)	3.3×10^{-4}	0	3	97	5.2×10^{-4}
	Marine reptile	5.8×10^{-4}	0	2	98	2.7×10^{-4}
	Marine mammal (dolphin)	5.8×10^{-4}	0	2	98	2.6×10^{-4}

TABLE 5.6. DOSE CONVERSION COEFFICIENTS FOR FRESHWATER REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE

Nuclide	Reference organism	Internal exposure				External exposure
		DCC ($\mu Gyh^{-1} \cdot Bq^{-1} \cdot kg$)	f_1 (%)	f_2 (%)	f_3 (%)	DCC ($\mu Gyh^{-1} \cdot Bq^{-1} \cdot L$)
^{226}Ra	Freshwater phytoplankton	2.9×10^{-8}	99	0	1	1.5×10^{-2}
	Freshwater zooplankton	1.4×10^{-2}	99	0	1	1.4×10^{-3}
	Freshwater crustaceans	1.4×10^{-2}	98	0	2	1.3×10^{-3}
	Freshwater insect larvae	1.4×10^{-2}	98	0	2	1.3×10^{-3}
	Freshwater plant (vascular plant)	1.4×10^{-2}	98	0	2	1.3×10^{-3}
	Freshwater gastropod	1.4×10^{-2}	97	0	3	1.1×10^{-3}
	Freshwater mollusc (bivalve mollusc)	1.4×10^{-2}	96	0	4	1.0×10^{-3}
	Freshwater pelagic fish (trout)	1.4×10^{-2}	95	0	5	9.2×10^{-4}
	Freshwater benthic fish	1.4×10^{-2}	95	0	5	9.1×10^{-4}
	Freshwater mammal (muskrat)	1.4×10^{-2}	95	0	5	8.3×10^{-4}
	Amphibian (frog)	1.4×10^{-2}	96	0	4	1.0×10^{-3}
	Wading bird (duck)	1.4×10^{-2}	95	0	5	9.0×10^{-4}
^{228}Ra	Freshwater phytoplankton	2.1×10^{-10}	0	9	91	8.4×10^{-4}
	Freshwater zooplankton	1.2×10^{-4}	0	7	93	7.2×10^{-4}

TABLE 5.6. DOSE CONVERSION COEFFICIENTS FOR FRESHWATER REFERENCE ORGANISMS FOR ^{226}Ra AND ^{228}Ra FOR INTERNAL AND EXTERNAL EXPOSURE (cont.)

Nuclide	Reference organism	Internal exposure				External exposure
		DCC (μGyh$^{-1}\cdot$Bq$^{-1}\cdot$kg)	f_1 (%)	f_2 (%)	f_3 (%)	DCC (μGyh$^{-1}\cdot$Bq$^{-1}\cdot$L)
	Freshwater crustaceans	1.6×10^{-4}	0	6	94	6.9×10^{-4}
	Freshwater insect larvae	1.6×10^{-4}	0	6	94	6.8×10^{-4}
	Freshwater plant (vascular plant)	1.8×10^{-4}	0	5	95	6.6×10^{-4}
	Freshwater gastropod	2.7×10^{-4}	0	3	97	5.7×10^{-4}
	Freshwater mollusc (bivalve mollusc)	3.1×10^{-4}	0	3	97	5.4×10^{-4}
	Freshwater pelagic fish (trout)	3.5×10^{-4}	0	3	97	5.0×10^{-4}
	Freshwater benthic fish	3.5×10^{-4}	0	3	97	4.9×10^{-4}
	Freshwater mammal (muskrat)	4.0×10^{-4}	0	2	98	4.5×10^{-4}
	Amphibian (frog)	3.0×10^{-4}	0	3	97	5.5×10^{-4}
	Wading bird (duck)	3.6×10^{-4}	0	3	97	4.9×10^{-4}

5.2.3. Non-homogeneous distribution

The DCCs for internal absorbed dose rate are calculated assuming a homogeneous distribution of radionuclides within the body. However, this is often not the case. For example, iodine accumulates in the thyroid, transuranic elements in the kidney and Ra in the skeleton. The influence of inhomogeneous distributions on the average whole body dose was investigated by Gomez-Ros et al. [5.11]. The analysis showed that uncertainties of the whole body DCC due to non-homogeneous radionuclide distribution are less than 30% for photons and electrons for all organisms considered. For electrons, the uncertainties are negligible below threshold energy, dependent on the size of the organisms. For α emitters, due to the short range, the average whole body dose is not affected by the distribution of the radionuclides.

In the case of accumulation of a radionuclide in a specific organ, the dose to the organ will be higher than the average of the whole body. The dose in a specific organ is enhanced by a factor that can be estimated from the ratio whole body mass / organ mass. For α emitters such as ^{226}Ra, this approximation is very accurate due to the short range of α particles. For ^{228}Ra (including the short lived daughter ^{228}Ac), both β and γ radiation contribute to the dose, and in this case this approximation is less accurate.

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Chapter 6

MITIGATION AND REMEDIATION ISSUES

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6.1. APPROACH TO IDENTIFY MITIGATION AND REMEDIATION MEASURES

As a result of former activities or accidents, but also of ongoing undertakings, Ra may have been or may continue to be dispersed in the environment. Thus, anthropogenically enhanced concentrations of Ra can be found in water, sediment and soil. Elevated concentrations may also be of natural origin.

All these situations may call for mitigation or remediation measures or both. Identification of the appropriate measures to mitigate the dispersion of Ra, to arrive at water concentrations below given limits or to remediate contaminated sites is as a rule a site specific process. Decision making in environmental remediation projects requires consideration of trade offs between sociopolitical, environmental and economic impacts and is often complicated by the various views of interested parties. Multi-criteria decision analysis emerged as a formal methodology to address available information and the values of interested parties to support environmental and human health decision making [6.1, 6.2]. In this process, the following aspects will ideally be considered:

- The source of Ra releases, for example, U mining and processing activities, mine flooding, residues from mining and processing activities, residues from water treatment, water discharged from treatment plants with remaining elevated Ra concentrations, NORM;
- Point source versus fugitive releases, dynamics of dispersion, factors driving the dispersion (climate, hydrological as well as hydrogeological and geochemical site conditions);
- Type of media of concern (drinking water, surface water, groundwater, sediments, soil, air);
- Level of contamination (low, moderate, high), scale and duration of contamination (volumes of contaminated material, areas affected, liquid effluent fluxes);

- Possibility of the presence of other radionuclides or other hazardous substances with a greater impact on the selection of mitigation and remediation measures;
- Site specific exposure pathways;
- Options at or near the site for the disposal or safeguard of contaminated material (soil, processing residues, NORM);
- Legal requirements on a national level (soil protection guidelines, mining acts, radiation protection ordinances, groundwater protection acts, drinking water guidelines, etc.);
- International guidelines and standards (set for instance by the ICRP, the IAEA or the World Health Organization);
- The involvement of interested parties, in particular when it comes to decisions regarding site rehabilitation alternatives;
- Financial costs, discount and net present values associated with each remediation alternative.

The following sections give advice on how to control and abate the dispersion of Ra into the environment. For different categories of sources and media, best available technologies are reported together with the advantages and disadvantages of their implementation. The implementation of the best available technologies listed below may not always be possible depending on site specific considerations such as financial costs, social acceptability, environmental impacts or human health issues. As a result, the best technologies screened for further consideration in selecting the final treatment alternatives are called best practicable technologies.

6.2. REMOVAL OF RADIUM FROM DRINKING WATER

The World Health Organization has issued Guidelines for Drinking Water Quality wherein a reference dose level of the committed effective dose equal to 0.1 mSv from 1 year’s consumption of drinking water is recommended [6.3, 6.4]. The European Commission (EC) [6.5] has set the same level of 0.1 mSv/a as a screening value for the monitoring of radiation in drinking water. The value is also called the total indicative dose and serves as a measure for the committed effective dose through drinking water. If gross alpha and gross beta measurements for drinking water show values below 0.1 Bq/L and 1 Bq/L, respectively, the total indicative dose is not exceeded and further radiological examination of the water is not required [6.5].

Neither the WHO nor the EC explicitly report maximum concentration limits for ^{226}Ra and ^{228}Ra. However, using dose coefficients proposed by the

ICRP [6.6–6.8], and taking into account a consumption rate of 730 L/a for adults and the 0.1 mSv/a reference dose level, secondary activity concentration levels of 0.49 Bq/L for ^{226}Ra and 0.20 Bq/L for ^{228}Ra, respectively, may be deduced. A given mixture of nuclides in the drinking water, with C_i as the concentration of the nuclide i, requires application of the summation formula (SUM $[C_i/MCL_i] \leq 1$).

In the United States of America, the Environmental Protection Agency stipulate maximum concentration limits for drinking water of 5 pCi/L (0.185 Bq/L) for ^{226}Ra and ^{228}Ra combined [6.9]. In Germany, values of around 0.125 Bq/L and 0.020 Bq/L for ^{226}Ra and ^{228}Ra, respectively, were set as maximum admissible concentrations in mineral water if the water is used for preparation of baby food [6.10]. In Canada, the maximal acceptable concentration for ^{226}Ra was set at 0.5 Bq/L [6.11].

Public water supply systems derive their water from surface water bodies such as rivers, streams and reservoirs, or from underground sources through drilled wells. Vast amounts of drinking water are obtained underground each year. For example, the fraction of drinking water obtained from groundwater in 1995 in Germany, France, Italy, Spain and the United Kingdom was 65, 60, 50, 20 and 25%, respectively [6.12]. Although natural radionuclides are also found in surface water, groundwater is more likely to contain higher levels of natural radiation due to the difference in chemical composition. The concentrations of naturally occurring radionuclides in groundwater will vary depending on the local geology. For example, higher concentrations can be found in granite and other U and Th bearing geological media. Hence, the predominant radionuclides found in groundwater include U, Ra, Rn and their decay products.

Surface waters used for drinking water show significantly elevated radionuclide concentrations only when they are impacted by anthropogenic sources, for instance, by effluents from U mining legacies or operations not properly regulated or managed. For example, a study in Germany revealed that only very few water suppliers (0.1%) are faced with the need to remove Ra from drinking water which comes from surface waters [6.13].

In most developed countries, public water suppliers are required to limit the occurrence of contaminants such as metals and pesticides, and sometimes also radiation in drinking water [6.4, 6.5, 6.11, 6.14–6.16]. Some waters may require treatment to reduce concentrations to levels accepted by the regulators concerned. One problem with water treatment is that the main processes that are designed to remove radionuclides from the finished product — drinking or process water — concentrate those radionuclides in filters and sludges, and contaminate filtration equipment. The now contaminated equipment may require treatment and cleaning, and the concentrated waste, residual sludges, filters and other residues require appropriate disposal. Even in cases where radionuclide concentrations are significant, but not above relevant standards, the customary water treatment, for example to remove hardness, can result in the accumulation of NORM in process residues [6.17, 6.18]. Technical options and methods for the treatment and safe disposal of residues from water treatment are presented in Section 6.10.

Table 6.1 summarizes the best available technologies for the removal of Ra from drinking water, together with their main advantages and disadvantages (see for instance Refs [6.19–6.23]).

TABLE 6.1. BEST AVAILABLE TECHNOLOGIES FOR RADIUM REMOVAL FROM DRINKING WATER: ADVANTAGES AND DISADVANTAGES

Best available technology	Process background	Advantage	Disadvantage
Sodium cation exchange	2 RNa + Ra2+ → Ra2Ra + 2Na+ - Electrostatic interaction between ions in solute and surface charge of resin	- Very pure effluents achievable - compact, small systems	- Brine solution obtained must be handled/disposed of - competing ions may influence performance
Lime softening	- Quicklime or CaO is added to form an insoluble calcium carbonate (CaCO3) precipitate, thereby co-precipitation of Ra - Flocculants assist flake formation and settlement in clarifiers	- Practicable at sites requiring high water treatment rates - Simple - Usually low cost	- High sludge production rates (disposal problem) - Depending on water hardness very low discharge concentrations may not be achievable
Reverse osmosis	- Removes ions by applying pressure to the water when it is on one side of a semipermeable membrane - The solute is retained on the pressurized side of the membrane and the pure solvent passes	- Very pure effluents achievable - Small, compact, modular plants	- Scaling (precipitates due to oversaturated solutions) and fouling (microbial growth) calls for intensive maintenance - High investment costs - Energy consumption - Brine disposal can be problematic

TABLE 6.1. BEST AVAILABLE TECHNOLOGIES FOR RADIUM REMOVAL FROM DRINKING WATER: ADVANTAGES AND DISADVANTAGES (cont.)

Best available technology	Process background	Advantage	Disadvantage
Green sand filtration	- Adsorption of Ra at the sand filter	- Simple - Low cost - Practicable at sites of high water rates	- Filter clogging / disposal of large filter volumes - Depending on water consistence, very low discharge concentrations may not be achievable
Sorption on MnO2, Ba-Ra-SO4 co-precipitation	- Use of manganese fibre absorbers (loose fibres or cartridge units) - alternatively, adding BaCl2 to precipitate Ba(Ra)SO4	- Simple technical equipment/ facilities	- Until now no large scale applications for drinking water - Filter backwashing needed - Produces large amounts of sludge - Long term stability of Ba(Ra)SO4 is uncertain if disposed of in lakes

In multistep systems, or combinations of the above mentioned methods, the resultant efficiency of ^{226}Ra removal can be appropriately improved. Coagulation, flocculation, aeration and filtration are often used in multistep systems, or combinations of the above mentioned methods, the resultant efficiency of ^{226}Ra removal can be appropriately improved. Coagulation, flocculation, aeration and filtration are often used in addition to facilitate the precipitation of suspended particles onto which the Ra is bound by the primary chemical or technical process. For instance, aeration of water promotes iron oxidation, iron oxide precipitation and with it the precipitation of Ra.

6.3. REMOVAL OF RADIUM FROM MINING AND PROCESSING WATERS

Surface and underground mines have varying potential to contaminate aquifers and surface water depending on the meteorological, hydrological and geological site characteristics. The potential of water contamination is not limited to U mining, although concentrations of U, Ra and other naturally radioactive elements are found in waters around these mines in particular. Significant contamination of mine water with Ra has also been reported, for instance, for sites of lignite coal mining [6.24, 6.25]. In fact, mine waters can be of environmental concern even a long time after mining operation has ceased [6.26–6.36].

Water is one of the main pathways by which natural radiation may be dispersed from mining operations into the environment. The quantity and chemical composition of mine water generated at mines vary by site and are dependent on the geochemistry of the ore body and surrounding area.

When ore is milled and the heavy metals are extracted by chemical processes, the resulting processing water may also have elevated concentrations of natural radionuclides. The same applies for water coming to the surface during the flooding of backfilled mines at the end of a mine life cycle (flowing drill holes).

Further, at mining and processing sites, U Th and/or Ra to a lesser extent, can be mobilized by either acidic or alkaline conditions. Many (sedimentary) rocks contain sulphidic minerals such as pyrite. Upon exposure to ambient air, these sulphides are oxidized to sulphuric acid [6.37]. These acidic conditions can accelerate the weathering of the mining debris and the dissolution and leaching of mineral constituents, including radionuclides, due to their higher solubility at low pH values [6.38, 6.39]. This phenomenon, known as AMD or ARD, is a worldwide problem and has been the focus of scientific and technical attention for some time (see Refs [6.37, 6.40]).

Elevated radionuclide concentrations have been reported frequently in AMD/ARD. For instance, ^{238}U and ^{226}Ra concentrations of 175 and 0.29 Bq/L, respectively, have been measured in the ARD of the U mining and milling facility of Poços de Caldas, Brazil [6.41]. Similar ^{238}U concentrations in the ARD of a coal mine in Brazil are reported by Eylander et al. [6.42], but saline waters from German hard coal mines have even higher Ra concentrations of up to 63 Bq/L of ^{226}Ra and up to 28 Bq/L of ^{228}Ra [6.43]. Elevated radionuclide concentrations due to ARD have also been reported downstream of the Rum Jungle and Rockhole U mines in northern Australia [6.44]. At the Lorado mill site in Northern Saskatchewan, acid generating tailings have lead to levels of ^{226}Ra ranging from 22 to 3230 Bq/L in groundwater, which feed into Nero Lake. Nero Lake has ^{226}Ra levels of 0.2 Bq/L in surface water with pH 3.58–4 [6.45]. This site operated from 1957 to 1960, a period when modern regulatory controls were not in place. Decommissioning plans are being developed and will be implemented in the next few years.

In a neutral or alkaline environment, carbonate minerals, organic carbon and carbon dioxide may also influence the migration of radionuclides. Calcite in mining debris can affect the movement of the acid front and precipitate ^{226}Ra with other metals. When sulphates are produced, gypsum may precipitate and remove some ^{226}Ra as a co-precipitate [6.46]. Organic matter and humic materials are additional pools that can strongly bind Ra [6.39].

At in situ leaching mining sites, well patterns are intended to create a hydrodynamically well controlled flow regime for the lixiviant, thus minimizing dispersion losses and the contamination of surrounding aquifers. Nevertheless, in situ leaching processes may result in the development of contaminated water plumes that extend beyond the boundary of producing well fields. Examples of this have been reported in the copper and U mining industries [6.47, 6.48]. The contaminants most often found in groundwater that exceed the drinking water contaminant limits include U, Ra, Se, Mo, Mn, nitrate, sulphate and As.

Prior to being discharged, mining and processing water may need to be treated depending on the level of natural radionuclides and other hazardous substances (e.g. Ni, Mo, Se, As, salts) in the water. Maximum admissible concentrations of Ra and other pollutants in released mining and processing water may be different from drinking water guidelines, depending on regulations, the site specific dispersion and the potential exposure pathways of the discharge site. In addition, water treatment requirements differ depending on whether water is directly released to the environment or used for drinking purposes. As a result, in addition to the options to remove Ra from drinking water, other water treatment technologies are also available. Table 6.2 [6.19, 6.25, 6.49–6.55] lists the best available technologies for the Ra removal from effluents at mining and processing sites.

6.4. REMOVAL OF RADIUM FROM CONTAMINATED GROUNDWATER

Groundwater contaminated with Ra can be found at U mining sites if seepage from waste rock piles, tailings management facilities or leaching fields is not properly intercepted. At sites that have been remediated prior to the 1990s, contaminated water plumes propagate beyond the boundary of the sites and fields (cf. for instance Refs [6.46, 6.56]). Flooding of U mines may also be associated with the propagation of Ra into adjacent aquifers [6.57, 6.58]. Furthermore, elevated Ra concentrations may occur in groundwater at coal mining sites [6.24]. The Ra mobilization depends on the source characteristics (volume, Ra specific activities, local geological and hydrological conditions at the sites, climate, etc. [6.59] as well as on the groundwater chemistry, in particular on the pH and the salinity of the groundwater [6.60].

Contaminated groundwater may be remediated in situ as well as off-site [6.61, 6.62]. Off-site remediation requires the pumping of the water to the surface

TABLE 6.2. BEST AVAILABLE TECHNOLOGIES FOR REMOVAL OF RADIUM FROM MINING AND PROCESSING WATER: ADVANTAGES AND DISADVANTAGES

BAT option	Process background	Advantage	Disadvantage	Reference
$Ba(Ra)SO_4$ co-precipitation	– Adding of $BaCl_2$ to SO_4^{2-} rich mine water to form insoluble Ba-Ra sulphate precipitates; – Flocculants assist flake formation and settlement in clarifiers.	– Able to treat high fluxes of mine water. • Simple; • Low costs.	– Large volumes of sludges are produced which require safe disposal; – Long term stability of $Ba(Ra)SO_4$ is uncertain when disposed of in lakes.	[6.19, 6.25, 6.49, 6.50]
Ion exchange	– Electrostatic interaction between ions in solute and surface charge of resin; – If only Ra has to be removed (which is as a rule not the case): sodium ion exchange $2RNa + Ra^{2+} \rightarrow Ra2Ra + 2Na^{+}$	– Compact systems (as a rule used to remove U; Ra is thereby partly also removed).	– Large initial investment and high operation costs; – Regeneration brine must be handled/disposed of; – Competing ions may influence performance.	[6.51]
Reverse osmosis	– Physical membrane separation technique where an applied pressure greater than the solution's inherent osmotic pressure is directed upon a semipermeable membrane which results in: • a purified permeate stream containing 2–8% of total dissolved solids; and • (b) a brine which retains the bulk of the dissolved solids and is an effluent by-product.	– High removal efficiency; – Not only specific to Ra but also to other nuclides.	– High investment and operating costs; – Stringent pretreatment requirements associated with the level of suspended solids in the feedwater.	[6.19, 6.51]

TABLE 6.2. BEST AVAILABLE TECHNOLOGIES FOR REMOVAL OF RADIUM FROM MINING AND PROCESSING WATER: ADVANTAGES AND DISADVANTAGES (cont.)

BAT option	Process background	Advantage	Disadvantage	Reference
Selective membrane mineral extraction	– Membrane components physically remove Ra with a chemical process to produce sludge containing Ra and a purified barren solution	– High removal efficiency; – Does not use Ba, other heavy metals or alternate sulphate precipitation methods – Partial reduction of salinity.	– Sludge produced needs to be handled carefully because of enriched Ra.	[6.51]
Nanofiltration	– This technique can be seen as a coarse reverse osmosis membrane. – Because nanofiltration uses less fine membranes, the feed pressure of the NF system is generally lower compared to reverse osmosis systems.	– Membranes do not require regeneration; – Absence of sludge formation which is contaminated and requires disposal; – Also the fouling rate is lower compared to reverse osmosis systems.	– Limited industrial usage but gaining popularity in recent years	[6.52]
Constructed wetlands	– Combination of biological and conventional treatment technologies (for instance iron oxidation through aeration, thereby co-precipitation of Ra, in addition: phyto-remedial measures [Ra uptake by macrophytic alga (Caraceae)], sand filters, technical filters).	– Low specific treatment costs; – Low maintenance and operation costs.	– Not applicable for primary and secondary treatment nor for treatment of high water fluxes; – Produced organic radioactively contaminated residues are problematic to dispose of; – Long term performance is uncertain	[6.53–6.55]

with subsequent treatment (‘pump and treat’). The technologies applicable to the above ground removal of Ra from groundwater are in principle the same as the best available technologies described in Section 6.3. However, in many cases Ra is only one of the elements to be extracted from the contaminated groundwater which has been pumped to the surface. The water may carry significant Mn or Fe load, or both. In more oxidizing situations, above ground Ra may co-precipitate with the Mn/Fe oxides [6.63].

An effective way to prevent the groundwater borne dispersion of Ra is the installation of permeable reactive barriers [6.61–6.64]. The most commonly used configuration of permeable reactive barriers is that of a continuous trench in which the treatment material is backfilled. The trench is constructed perpendicularly to and intersects the groundwater plume. A funnel and gate construction with impermeable walls guiding the influent water through the permeable barrier results in a higher efficiency of water catchment. To remove Ra from the groundwater, an appropriate treatment media in the barrier is sand mixed with $BaCl_2$; the chemical process of immobilization of Ra in the wall in this case is Ba Ra sulphate precipitation. The advantages of permeable reactive barriers are: in situ remediation, passive operation, no above ground structures required, and the potential to be less expensive than pump and treat systems in the long term. The exhausted barrier material has to be replaced and disposed of at a suitable engineered disposal facility [6.61].

6.5. REMOVAL OF RA FROM SOIL

Radium nuclides are found in almost all soil materials in background concentrations which vary from site to site, depending on local geological conditions. The IAEA and the EC have recently recommended exemption and clearance levels for all radionuclides in the decay chain of ^{238}U or ^{232}Th, including ^{226}Ra and ^{228}Ra [6.67, 6.68]. An exemption or clearance level of 1 Bq/g has been determined for naturally occurring radionuclides in solid materials in secular equilibrium with their progeny for all nuclides of the ^{238}U and ^{232}Th decay chains. However, this value does not apply for the specific activity of Ra (^{226}Ra, ^{228}Ra) and Th nuclides in building materials (see Section 6.6). It also does not apply for conditions where large volumes of soil with elevated specific activities of ^{226}Ra may cause significant radon exposure (see Section 6.9).

Soil specific activities of ^{226}Ra and ^{228}Ra above 1 Bq/g may justify remedial measures, provided they are caused by human activities, i.e. they represent an anthropogenic contamination. Soil contaminated with Ra is found, for instance, at mining and processing sites [6.59, 6.69], or at sites where water with elevated Ra concentrations has spread into the environment [6.70, 6.71]. In countries with sites heavily contaminated by former U mining and milling activities, national standards have been stipulated for each site cleanup (e.g. Refs [6.72, 6.73]).

There are in situ options as well as off-site options for the removal of Ra. A modern option for the removal of Ra from soil on a site is phytoremediation. This technology is based on the capability of plants to extract Ra from soil and accumulate it in compartments of the plant [6.74–6.76]. In wet environments, Ra uptake by macrophytic algae (*Characeae*) is a possibility [6.54, 6.55]. This method is usable to rehabilitate small to medium sized areas. However, the uptake process is time consuming. An essential shortcoming of the method is that it results in contaminated biota (plants) which require further handling as radioactively contaminated material. The final disposal of such substances is problematic or may become expensive, in particular with respect to the need to immobilize the radiation and radionuclides at the disposal site. Biomaterial in disposal facilities requires special technical barriers to prevent mobilization and dispersion of heavy metals and other hazardous substances from the site.

Other technologies for the removal of Ra from soil, such as the in situ washing of soil or the excavation of the soil with subsequent purification at a special treatment site (off-site washing) have not yet been described in the literature as useful options for Ra. Consequently, complete removal of the contaminated soil and disposal of the material at an engineered site is a common procedure, provided the soil volume is not excessive. However, if large volumes of soil are contaminated, then in situ remediation of the site is the best practice (see Sections 6.8 and 6.9).

6.6. CONTROL OF RADIUM IN THE BUILDING INDUSTRY

Building materials can show elevated concentrations of natural radionuclides, including ^{226}Ra and ^{228}Ra. This can be of natural origin, when the radiation is already contained in the raw material (e.g. natural stone), or it can be due to the addition of industrial products (e.g. zircon sand), intermediates or by-products (e.g. coal ash, phosphogypsum and furnace slags) of the raw building material. Recycling of industrial residues and wastes in this manner has been encouraged for reasons of minimizing resource use and is often favoured by industry since it adds value to a material for which otherwise disposal costs might arise. Concern has risen, however, over the potential content of radiological and other contaminants in the recycled materials. Owing to the wide variety of raw and recycled materials and their possible NORM content, no general data are presented here. The NORM content in natural resources may also vary considerably over short distances, for example in granite quarries [6.77].

The majority of radiological investigations published in the international literature on building materials are concerned with scenarios of residential exposure, i.e. gamma, radon and, in some cases, thoron exposure of the inhabitants. Some studies and estimates are available on occupational exposures in some particular industrial working environments [6.76, 6.78], and for construction work [6.79].

Table 6.3 gives a summary of ranges of reported values for Ra concentrations in building materials as final products. The table was constructed using a compilation of data from European Union member and non-member states [6.80] as well as a range of European and international papers [6.77]. It is worth noting that activity concentration values of the ^{238}U chain in building materials are generally published as ^{226}Ra concentration, but sometimes also as ^{238}U. The data in Table 6.3 [6.77] cannot be expected to provide a statistically representative picture of the situation for two reasons: firstly, because very few nationally representative investigations have been made in different countries; secondly, because analytical efforts are typically focused on samples and materials that are expected to show high activity concentrations.

TABLE 6.3. ACTIVITY CONCENTRATIONS OF NATURAL RADIONUCLIDES IN BUILDING MATERIALS (BQ/KG)

Building material	^{226}Ra
Concrete	1–250
Aerated and lightweight concrete	9–2200
Clay (red) bricks	1–200
Sand lime bricks and limestone	6–50
Natural building stones	1–500
Natural gypsum	<1–70
Cement	7–180
Tiles (glazed and unglazed)	30–200
Phosphogypsum (plasterboard)	4–700
Blast furnace slag stone and cement	30–120

More than 280 Mt of coal ash (fly ash and bottom ash combined) are produced annually. About 40 Mt of these are used in the production of bricks and cement [6.81]. Since most of the process residues which are further processed into building materials do not meet the required technical specifications, they are typically mixed with pristine raw materials. The net effect is a dilution of the NORM content relative to the process residues.

The dominating exposure pathways due to elevated specific activities of ^{226}Ra in building materials are exposure by external irradiation and exposure by inhalation of radon and its short lived daughter nuclides.

In 1996, it was estimated that up to 15% of phosphogypsum was recycled and that within the European Union some 2 Mt were recycled annually [6.82]. Its activity concentration depends on the origin and the chemical treatment of the raw material. For example, phosphogypsum from phosphate rocks generally contains considerably higher concentrations of ^{226}Ra than gypsum from carbonate rocks. In any case, not only the Ra concentration but also the radon exhalation from it can be higher than background [6.80].

Blast furnace slags are used mainly as aggregate with concrete (crushed) as well as an additive in cement (finely ground). The activity concentration in the slags depends on the ore type, the origin of the raw material and the metallurgic processes. The use of (coal) fly ash and slags in concrete is a well recognized source of gamma exposure that is due to the presence of activity concentrations of ^{226}Ra, ^{232}Th and, to a lesser extent, ^{40}K, while the exposure via radon exhalation is lower than could be expected from the ^{226}Ra content, due to the low emanation coefficient from the ash [6.83]. Phosphogypsum and gypsum from flue gas desulphurization used, for example, in the production of plasterboard, may give rise to similar concerns.

Zircon flour is used in the ceramic and refractory materials industry, particularly for glazing tiles. The use of zircon sand as an opacifier in glazes for tiles does not seem to significantly increase the exposure of the general public to gamma radiation [6.84, 6.85] or to exhaled radon, owing to the typically relatively low ^{226}Ra concentrations [6.85] and low emanation factors from the glaze. However, measurements performed by some Chinese researchers in rooms with and without glazed tiles [6.84] showed that the average area density of total beta radionuclides in tile glaze was 12–13 times as much as that in ordinary building material. Similar results were obtained in another recent study from China [6.86]. This causes an increase in the external beta radiation dose received by the public in buildings and therefore a possible exposure pathway to the public from residues due to processing or possible waste material.

In Europe, the EC recommends the application of a summation formula to control natural radionuclides in building materials, including ^{226}Ra [6.87].

$$[C_{\text{Ra-226}}/(300\ \text{Bq/g}) + C_{\text{Th-232}}/(200\ \text{Bq/g}) + C_{K\text{-40}}/(3000\ \text{Bq/g})] < I \qquad (6.1)$$

The EC guidance states a value of $I = 1$ for bulk material and a value of $I = 6$ for surface material and for other material of restricted use. If this formula is fulfilled, the external exposure for a 7000 h stay in a house (standard room geometry) remains below 1 mSv/a and the exposure by inhalation of radon is of minor significance [6.68, 6.87].

6.7. CONTROL OF RADIUM IN BIOTA

Monitoring programmes have been put into operation in many IAEA Member States to confirm whether the controls implemented to limit the releases of ^{226}Ra result in concentrations of radionuclides in biota below pre-determined dose benchmarks. Monitoring also includes measurements of other nuclides such as $^{238/234}$U, ^{210}Pb, ^{230}Th and ^{210}Po in soil, sediments and surface and groundwater. Such monitoring programmes are of particular importance in countries with large scale U ore mining, milling and processing or with large mining legacy sites still awaiting remediation. In cases where the monitoring programme indicates that maximum admissible concentrations have been exceeded (by a site specific exposure analysis), contingency measures are recommended to limit the transfer of Ra into biota and into the human food chain and to prevent the provision of contaminated food to the public.

6.8. REMEDIATION OF CONTAMINATED AREAS

The removal of Ra from soil has already been addressed in Section 6.5. However, depending on the total area impacted and on site specific conditions (location of the area in relation to potential exposure sites of the public, conditions governing the dispersion of Ra, concerns of interested parties, availability of disposal sites, etc.), other options for the remediation of a Ra contaminated area may be more efficient than the direct removal from soil. Table 6.4 gives an overview of the principal remediation options, including the advantages and disadvantages for their application. A comprehensive overview of site remediation technologies is given in Falck et al. [6.88] and in the proceedings of an international symposium on the remediation of radioactively contaminated sites organized by the IAEA [6.89].

TABLE 6.4. MAIN OPTIONS FOR THE REMEDIATION OF CONTAMINATED AREAS

Option	Process background	Advantages	Disadvantages
Complete removal of the contamination from the site	– Cleanup by excavation of all of the contaminated soil; –Refilling with inert material (recontouring) if needed; – Safe disposal of the contaminated soil.	– Unrestricted reuse of the cleaned area; – Most sustainable remediation option; – Will ideally be applied whenever achievable with reasonable effort.	– Expensive in cases of large affected areas or of dispersed heterogeneous contamination; – Requires release measurements; – Large volumes of contaminated material to dispose of; – May negatively impact local ecology.
In situ remediation by coverage and revegetation	– Minimization of rainwater infiltration, thus reduction of Ra releases via seepage; – Minimization of radon exhalation; – Minimization of the gamma dose rate.	– Cost effective in cases of large contaminated areas or management of large volumes (see Section 6.9).	– Permanently restricted reuse of the area, i.e. not a very sustainable option; –Ongoing maintenance required and reliance on institutional controls.
Minimizing the dispersion of Ra via groundwater from a contaminated site	– Cutting dispersion pathways by impermeable barriers; – Removal of Ra from the water plume by semipermeable reactive barriers.	– Easy to install and particularly effective in cases of local, non-extensive contaminations.	– Only effective in combination with other methods (cover); – Reactive barriers need maintenance and recovering of the wall; the latter results in contaminated material to dispose of.

TABLE 6.4. MAIN OPTIONS FOR THE REMEDIATION OF CONTAMINATED AREAS (cont.)

Option	Process background	Advantages	Disadvantages
Minimizing the entrance of water into bulk contamination (installation of drainage and water diversion systems)	– Preventing the entrance of upstreaming groundwater (construction of a drainage ditch or an impermeable wall); – Drainage of surface water.	– Easy to install (N.B.: surface water diversion is as a rule part of the cover construction).	– Only effective in combination with other methods (cover); – Technical barriers require maintenance.
Relocation of material from different sites (local contaminations) to one site, in situ remediation of the collected material	– Minimization of the contaminated area by remediation of sites with dispersed or distributed (spot) contaminations).	– Reduction of the area with reuse restrictions; – Very useful at mining sites where radioactive mining and milling waste has been scattered in the environment.	– Not all areas are cleared for unrestricted reuse; – Post-remedial actions are needed at the site of waste storage (maintenance, monitoring).
Phytoremediation	– Capability of plants to extract Ra from soil.	– Simple; – Low cost.	– Only for small sized areas; – Long term performance unknown; – Production of biological waste (cf. Section 6.5); – Not suitable for urban areas.
Natural attenuation (do nothing option)	– Sum of all physical, chemical and biological processes promoting the dispersion of the contamination from the site (dilution process).	– Costs only for monitoring of the process; – No maintenance.	– Long term restricted reuse of the affected land; – Although dilution leads to a lower level of contamination, the affected area becomes expanded; – Not applicable to or only limited applicability in urban areas.

Reliance on natural attenuation to remediate mine sites contaminated by ^{226}Ra can only be considered in cases where a multicriteria decision analysis [6.2] performed in a transparent and rigorous manner has indicated that natural attenuation is the best practicable alternative. Or, in some situations, natural attenuation may be the best practicable alternative for remediation of some areas of mine sites while other areas could be remediated using the best practicable technologies. For instance, if an abandoned mine site was left alone for decades, during which loading of ^{226}Ra to a lake occurred and led to widespread sediment contamination, it could be more practicable to treat the source of ^{226}Ra contamination and allow for clean sediments to naturally cover the sediments contaminated with ^{226}Ra if the extent of sediment contamination is such that remediation such as capping or removal would not be practicable.

6.9. MANAGEMENT OF SPECIAL WASTE ROCK AND RESIDUES FROM FORMER MINING AND MILLING ACTIVITIES

Special waste rock material (i.e. low grade ore, special waste rock that can generate acidity or neutral drainage with high concentrations of contaminants) from mining of U ore and the residues from the chemical processing of the U ores (so-called tailings) are major potential sources of Ra releases to the environment [6.46, 6.59]. The most effective ways of minimizing the release of Ra from special waste rock piles and milling residues is to keep the production of these Ra containing materials low, mainly through application of low waste generation technologies. Further, for special waste rock and tailings, the selection of appropriate disposal sites and the installation of technical barriers (impoundment construction, in-pit disposal) at these sites are important ways to minimize the release of Ra. This is addressed in detail in Ref. [6.90], and will therefore not be discussed in this report. More emphasis is therefore given in the following to the management at a site of already existing special waste rock materials and tailings from past activities.

In waste rock piles at U mining sites, the specific activity of ^{226}Ra is in a range of 0.3–166 Bq/g, in radioactive equilibrium with the parent nuclides as well as with the decay nuclides [6.91–6.93]. As a result of weathering and leaching processes, minor disequilibria are, however, observable. Owing to the volumes of waste rock piles, which are often large, severe radiological impacts on the environment and the local public may be caused even in cases when the mean specific ^{226}Ra activity of the waste rock material is below 1 Bq/g (see the exemption level discussed in Section 6.5). As a rule, the exhalation of radon from waste rock piles is the main contributor to the radiation exposure of people living close to the piles [6.94, 6.95].

In residues from the chemical processing of U ores, ^{226}Ra is an important radionuclide from a radiological impact viewpoint. Specific ^{226}Ra activities range from a few Bq/g up to 20 Bq/g, with values up to 700 Bq/g having been reported [6.96]. Radium-226 in tailings generally occurs in a mixture with other, mainly chemotoxic substances, in a 'harsh' chemical environment (including extreme pH values of the pore and drainage water). Elevated gamma dose rates at tailings dams, radon exhalation, wind erosion with propagation of dust born long lived alpha emitters and the seepage of water containing Ra out of the tailings may cause significant radiological hazards.

The management of U mining and milling residues or existing legacies from former operations is described in technical documents by the IAEA, cf. Refs [6.90, 6.97–6.99]. Many references can be also be found in the proceedings of a series of symposia on tailings and mine waste started at Colorado State University in 1978, cf. Ref. [6.100]. Further, the efforts in developing optimized remedial measures gathered over the last two decades have been reported at the periodically held meetings of UMREG, the Uranium Mining Remediation Exchange Group [6.92] unifying experts from Australia, Canada, the Commonwealth of Independent States (CIS), Europe and the United States of America. In Section 7.4, the large scale management of legacies from U mining and milling is exemplified by the Wismut case study describing ^{226}Ra related aspects of the remediation of former U production sites in the former German Democratic Republic, in the federal states of Saxony and Thuringia. The main technologies for remediation of sites affected by former U ore mining and milling are compiled in Table 6.5. Emphasis is thereby placed on the site specific application of the listed options.

TABLE 6.5. REMEDIAL OPTIONS FOR SITES WITH URANIUM MINING AND MILLING LEGACIES

Option	Process background	Advantage	Disadvantage
Special waste rock			
Relocation to a safe site (far from potential sites of exposure), bringing waste rock material from dispersed small piles together at one site	– Complete removal of contaminated material from the site; – Disposal of the material at a safe site; Above ground (safeguard by cover); Underground (small volumes).	– Source of Ra dispersion is removed from the site; – Unrestricted reuse of the formerly contaminated site becomes possible;	– Above ground disposal generates a new or enlarges an existing contaminated site.

TABLE 6.5. REMEDIAL OPTIONS FOR SITES WITH URANIUM MINING AND MILLING LEGACIES (cont.)

Option	Process background	Advantage	Disadvantage
In situ remediation by contouring, covering and revegetation	– Contouring to stabilize slopes (if needed); – Cover to reduce the gamma dose rate, the radon exhalation and the release of Ra with seepage water; – Revegetation to stabilize slopes, to regulate the cover water balance and to fit site into landscape.	– Cost effective solution for large amounts of waste rock material.	– Restricted reuse of the covered pile area; – Need for long term post-remedial actions (maintenance of drainage systems, monitoring); – Long term performance is uncertain.
Tailings material			
Relocation of tailings ponds (far from potential sites of exposure)	– Complete removal of contaminated material from the site; – Construction of a tailings management facility at the new site.	– Source of Ra dispersion is removed from the site; – Unrestricted reuse of the old site.	– Expensive, generates a new contaminated site which requires long term maintenance and control; – Short term exposure to workers.
Wet in situ remediation	– Tailings in an engineered impoundment are covered by supernatant water.	– Less expensive than other options.	– Only possible in regions with positive net water balance (non-arid conditions); – Dam structure needs to be maintained by institutional controls.
Dry in situ remediation by dam stabilization, stabilization of soft tailings, coverage and revegetation	– See: in situ remediation of waste rock piles, before placement of a cover soft tailings must be stabilized (solidification by water derivation, interim coverage).	– Compared to other options, fewer control and maintenance measures are required; – Restricted reuse of the site may become possible.	– Expensive; – Long lasting remediation activity.

Identification of the best option for the safe management of large scale legacies from former mining and milling is a complex process involving an iterative approach of gradual steps (see Fig. 6.1 [6.1, 6.91]).

As discussed in Section 6.1, multicriteria decision analyses [6.2] consider all aspects (e.g. engineering design, environmental impacts, social and economical factors) of the decommissioning of legacy mine sites. One of the first decisions that must be obtained from the multicriteria decision analysis is whether the wastes need to be relocated or remediated in situ. In both cases, the cover design is essential for the safe management of natural radionuclides in mining legacies, including the selection of appropriate cover materials [6.101, 6.102]. Both the design and the materials are governed by the site conditions and the local relevance of the exposure pathways. Thereby, the external gamma radiation in special waste rock piles and tailings dams, which is in a first approximation proportional to the ^{226}Ra specific activity, can be managed by placement of a simple 0.5 m thick cover of inert soil [6.103]. In contrast to the reduction of gamma dose rates, the reduction of the radon exhalation rate (the radioactive noble gas radon (^{222}Rn) is the decay nuclide of ^{226}Ra) as well as the reduction of the infiltration rate (which at least regulates the percolation of precipitation water through the tailings body and subsequently the release of Ra with seepage water) both require a sophisticated cover design [6.95, 6.104].

For waste rock piles with a low geochemical potential to mobilize water borne Ra, it is sufficient to only place a cover which abates the exhalation of

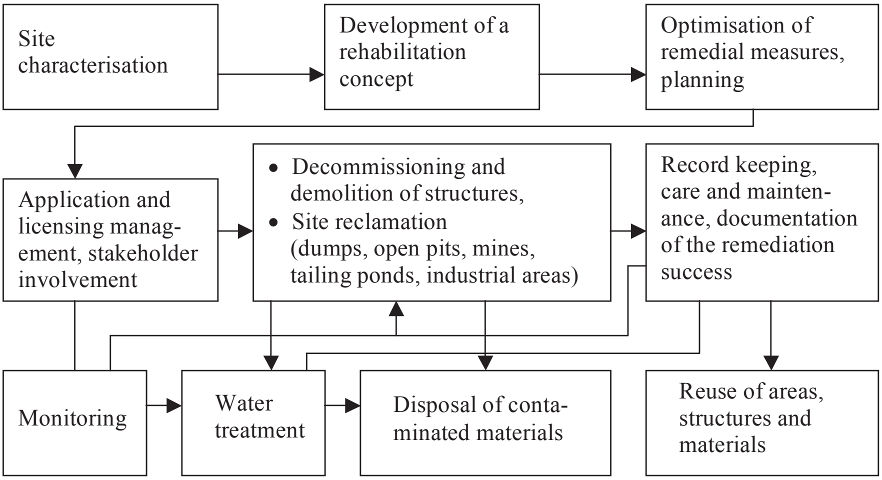

FIG. 6.1. Iterative approach to identifying optimized options for the management of large scale mining and milling residues [6.91].

radon. Typical radon barriers are at least 1 m thick and consist of a soil material with low gas permeability ($< 0.5 \times 10^{12}$ m²; i.e. fine grain sized soil [6.94, 6.105, 6.106].

For piles with a higher potential to mobilize Ra through the water pathway, and especially in tailings facilities, multilayer cover systems are placed. Such systems are designed to minimize the infiltration of rainwater. In areas with non-arid climate conditions, i.e. with a positive water balance where the precipitation rate exceeds the potential evaporation rate, the central element of such covers is a sealing layer which is built to minimize the water infiltration rate. The sealing layer is made of clay or till and the water permeability ought to be well below 10^{-9} m/s. A drainage layer and a water storage layer which regulate the water balance in the multilayer system are placed above the sealing layer [6.107, 6.108]. A drainage system to enable the runoff of precipitation water, perhaps in combination with a drainage system facing the upstream of groundwater, also contributes to the minimization of water infiltration. The detailed layer construction is driven by site specific conditions (climate, acidification potential of the tailings, hydrological conditions in the basement, soil conditions, short- and long term contaminant dispersion, etc.)

From a geochemical point of view, a common necessity is to avoid the acidification of the water in the tailings bulk by the prevention of pyrite oxidation and subsequent acidification of the percolation water. Acid water drainage may mobilize heavy metals. Therefore, the cover must have a low oxygen diffusion coefficient [6.109]. It is important to be aware that Ra release in seepage is only marginally impacted by the geochemical conditions, i.e. only technical barriers (sealing layer, drainage system) primarily trigger the Ra release from a tailings management facility.

In non-arid climate areas, a re-cultivation layer normally tops both the radon barrier type cover as well as the infiltration barrier type cover. This layer is dedicated to promoting plant growth on the cover. The construction and the material of the recultivation layer as well as the plants to be used have again to meet the local climate conditions. The plants will on the one hand ideally guarantee a positive water balance in the cover (by evapotranspiration and by the prevention of seasoning of the storage layer). On the other hand, the plant roots ought not to heavily affect the cover’s radon barrier ability in cases of a radon barrier type cover and ought not penetrate into the sealing cover in cases of an infiltration barrier type cover.

The selection of cover types is exemplified in Section 7.4, the Wismut case study.

6.10. MANAGEMENT OF NORM WITH ELEVATED RADIUM CONCENTRATIONS

NORM is produced in many technical processes and by the application of a variety of technologies dedicated to removing natural radionuclides from environmental media or equipment. Well known examples of NORM are sludges and scales from the oil and gas industry, and residues from water treatment. Radium-226 and -228 are the predominant nuclides in NORM, in particular when the specific activities and the concentrations of the natural radionuclides have been enhanced by technological processes [6.110, 6.111].

Many principles for the management of NORM are similar to those which apply for the management of residues from the mining and milling industry. In both sectors, Ra is a key element when it comes to assessing radiological impacts. For example, in the oil and gas industry ^{226}Ra and ^{228}Ra dominate the radionuclide vector in scale (encrustations in pipes) and in sludges (accumulated in separators, valves, etc.), and specific activities of up to several hundreds of Bq/g are reported (see for instance www.ean.net, the web site of the European ALARA Network on NORM). The Ra isotopes may also be important contaminants in residues from water treatment, and in the solid residues generated by the exploration and development of geothermal systems [6.110, 6.111].

If large volumes of residues are produced (for instance, ashes containing natural radionuclides or filter sands), in situ safeguarding of the material by coverage is possible. In general, however, the residues are disposed of in ponds, landfill, underground facilities, beach areas of mill tailings ponds, engineered subsurface facilities or other storage facilities constructed to store radioactive waste.

A variety of methods are employed for the disposal of drinking water treatment sludge, including ponds, landfills, sewer systems, deep well injection and land spreading or soil conditioning, while the decanted water is recycled. Some of these practices, however, are now forbidden in certain Member States due to the resulting contamination with heavy metals.

The disposal of sludges in ponds results in the accumulation of Ra in the bottom sediments, which may have to be dredged and disposed of. In addition, evaporation is used in ponds as a means to reduce the volume of the waste. However, this results in a lower volume of residues with a higher specific activity of radionuclides. In cases where the concentrations of radionuclides are high, it may be necessary to dispose of the residues in a licenced radioactive waste disposal facility. Given that NORM is long lived, it may be a problem to dispose of these wastes in a near surface repository [6.112].

From a groundwater protection perspective, the disposal of sludges is likely to be the greatest concern, because the radionuclides on resins or filter media would not be expected to be as mobile. The use of evaporation ponds to dispose of residues may result in the contamination of underlying groundwater bodies. This may then require long term stewardship or other measures to prevent future human and environmental exposure due to migration, or due to reuse of the water or residues. The disposal of NORM containing residues into sanitary sewer systems can potentially result in accumulations of those radionuclides in sewage sludge. Depending on the concentration levels found in the sludge, special considerations may need to be given to the reuse or disposal of this waste.

While the vast majority of residues from water treatment are in the form of sludges, ion exchange resins and filter media can also be a significant radiological concern given that very high concentrations of Ra are possible in those residues. External exposure and potential radon exposures are likely to be of more concern for resins and filter media, because the concentrations of NORM would not be expected to decrease substantially over time.

Depending on the site specific features of the disposal site, residues showing high specific activities of ^{226}Ra and ^{228}Ra may require special precautions to prevent dispersal. For example, any brines or sludges stored in ponds have the potential for seepage into the ground, and hence for contamination of groundwater. Disposal of both scales and sludges into landfill facilities also has the potential for long term radionuclide transport through groundwater if a site liner fails.

One way to prevent dispersal is to embed the residues in a matrix which is resistant against leaching of Ra. In Germany, geopolymer has been successfully applied as an immobilization matrix material for Ra [6.113]. Conventional matrix materials such as cement , however, fail because sulphate-reducing chemical reactions in cement promote Ra elution. Other approaches are to place the Ra containing residues in special containments or to establish additional barriers (liners, asphalt, organic foils and drainage systems) to prevent Ra releases from the site. Owing to the long half-life of ^{226}Ra, these technical barriers must be stable in the long term (i.e. for thousands of years).

REFERENCES TO CHAPTER 6

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Chapter 7

CASE STUDIES

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7.1. RABBIT LAKE

The Rabbit Lake operation, which opened in 1975, is the longest operating U production facility in North America, and the second largest U mill in the world. The site is located in northern Saskatchewan, Canada, and comprises open pits from past mining, on-going underground mining, a mill, a water treatment facility and tailings management facilities. Recently, it has been proposed that this site process 4.6 million kg of U per year (5.4 million kg of U_3O_8 equivalent) from a separate site, the Cigar Lake mine, as a U solution.

An assessment was undertaken to evaluate the releases from the facility. The approach was to develop a conceptual site model that included the characterization of the existing environment as well as releases of radionuclides to the environment. The behaviour and fate of the radionuclides released to the environment are then modelled and an exposure pathway analysis is performed to estimate the exposures and doses to local biota and people. Finally, the estimated doses are compared to reference dose rates and regulatory dose limits.

This assessment was performed for a broad range of radionuclides including ^{210}Pb, ^{210}Po, ^{226}Ra and ^{230}Th, as this is required for dose calculations and in most cases is also included in the monitoring program required by the site licence. The case study summarized in this section describes the approach taken, the data used and the results, with a focus on ^{226}Ra. A full description of the study is provided in Ref. [7.1] (this study was performed not only for several radionuclides but also a wide range of other contaminants of concern).

7.1.1. Study approach

7.1.1.1. Physical environment

The Rabbit Lake operation is located on the west side of Wollaston Lake in northern Saskatchewan within the Northern Transition Section of the Boreal Forest Region. This area is characterized by a low floristic diversity which results from the adverse climate, shallow rooting depths, the thin soils of mixed sandy loam and a high fire frequency.

Wildlife habitat in the area is typical for boreal woodland. A young jack pine habitat dominates the immediate area and provides cover for small mammals as well as for many bird species. An abundance of nearby lakes and connecting drainages ensures the availability of riparian areas potentially important for moose. Wildlife populations and diversity can vary significantly within the boreal woodlands area. Woodland caribou and wolverine have ranges that overlap with the project area.

Background water quality in the lakes and streams are typical of Precambrian Shield watersheds. The pH values tend to be neutral to slightly acidic, controlled by bicarbonates. Hardness and conductivity tend to be moderately low and heavy metal concentrations and radionuclide levels are generally below detection levels or guidelines.

7.1.1.2. Conceptual site model

The treated water is released to Horseshoe Creek, which discharges to Hidden Bay on Wollaston Lake. Extensive bog and fen areas are common, particularly near the lower reaches of Horseshoe Creek.

The conceptual site model (Fig. 7.1) for the Rabbit Lake site displays a graphic overview of the relationship between the receptors, and of the physicochemical processes that are occurring which affect the fate and transport of radionuclides (and chemicals). It also illustrates some of the food web processes that are occurring.

7.1.2. Receptor characterization

One of the key considerations which define the scope of a risk assessment is the selection of ecological and human receptors. This section provides a few comments on the selected receptors.

Non-Human Biota (Ecological Receptors). The first step in an ecological risk assessment is the determination of which ecological species to examine. It is not necessary to evaluate all species; ecological receptors are generally chosen to

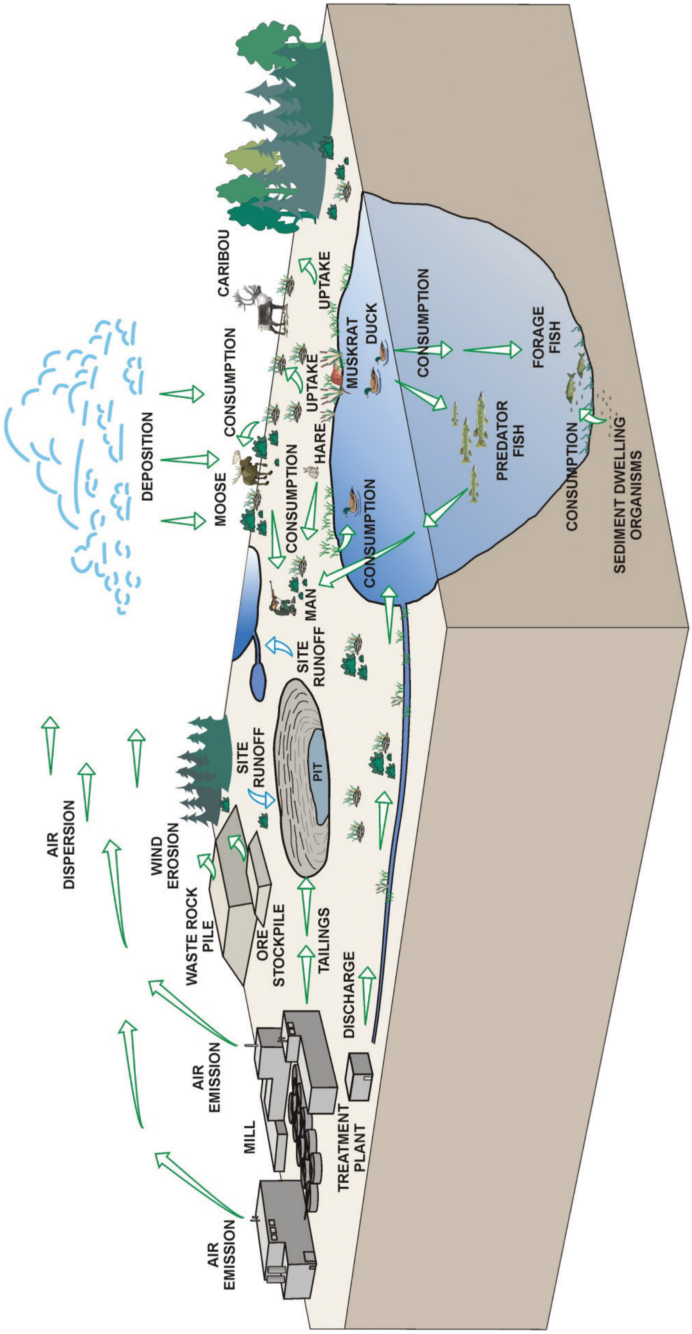

FIG. 7.1. Conceptual site model for the Rabbit Lake site. Note: The model is conceptual only. Not all exposure pathways for receptors are shown in the figure.

capture various types and magnitudes of exposure due to their different behavioural and dietary characteristics. In the Rabbit Lake assessment, primary exposure, as typical for a northern Canadian U facility, is via water pathways; thus, several ecological receptors were selected to capture exposure from drinking water and consumption of aquatic plants, fish, invertebrates and sediments. However, air emissions were also considered in the assessment, thus selected wildlife species that receive most of their exposure via atmospheric and terrestrial pathways were included. Species consumed by people in the Hatchet Lake Band [7.2] were also considered. The terrestrial receptors chosen for the current assessment represent a wide range of exposures and are presented in Fig. 7.2. Information on local species is provided in Ref. [7.2] and details on the range and diets of the receptors are provided in Ref. [7.1].

In selecting locations where terrestrial species were assumed to be present in the vicinity of the Rabbit Lake operations, factors taken into consideration included not only dietary characteristics but also the home range of the species and locations where the species would likely receive a range of exposures. An exemplary graphical depiction of ecological pathways for hare and ptarmigan, grouse, caribou and moose is provided in Fig. 7.3.

Human Receptors. Representative people were included in the assessment, such as: residents of the Wollaston Lake community, operators of a nearby fishing lodge, as well as an individual with a registered trap line in the area. Others were chosen to account for people who in the future could set up camps in close proximity to the decommissioned mine site. These human receptors are expected to obtain their dietary components (fish, which comprise a major portion of the local diet, moose, beaver, ducks, hare and ptarmigan) from the local area. Similarly, drinking water is obtained from Wollaston Lake while berries are picked from the local airshed. Barren-ground caribou are hunted for consumption in an area which is unaffected by the site emissions. The consumption of traditional food by the adult and child receptors was based on the Hatchet Lake Band dietary survey [7.2]. Non-nuclear workers, such as camp cooks or security guards, were also included and are only susceptible to respiratory pathways of exposure.

7.1.3. Risk assessment

Within the ecological risk assessment framework, assessment endpoints for ecological receptors are based on potential effects at population or community levels. Measurement endpoints are commonly selected at the individual level of biological organization, and are typically based on exposure responses that are meant to act as a proxy for population and community characteristics such as reproduction and abundance.

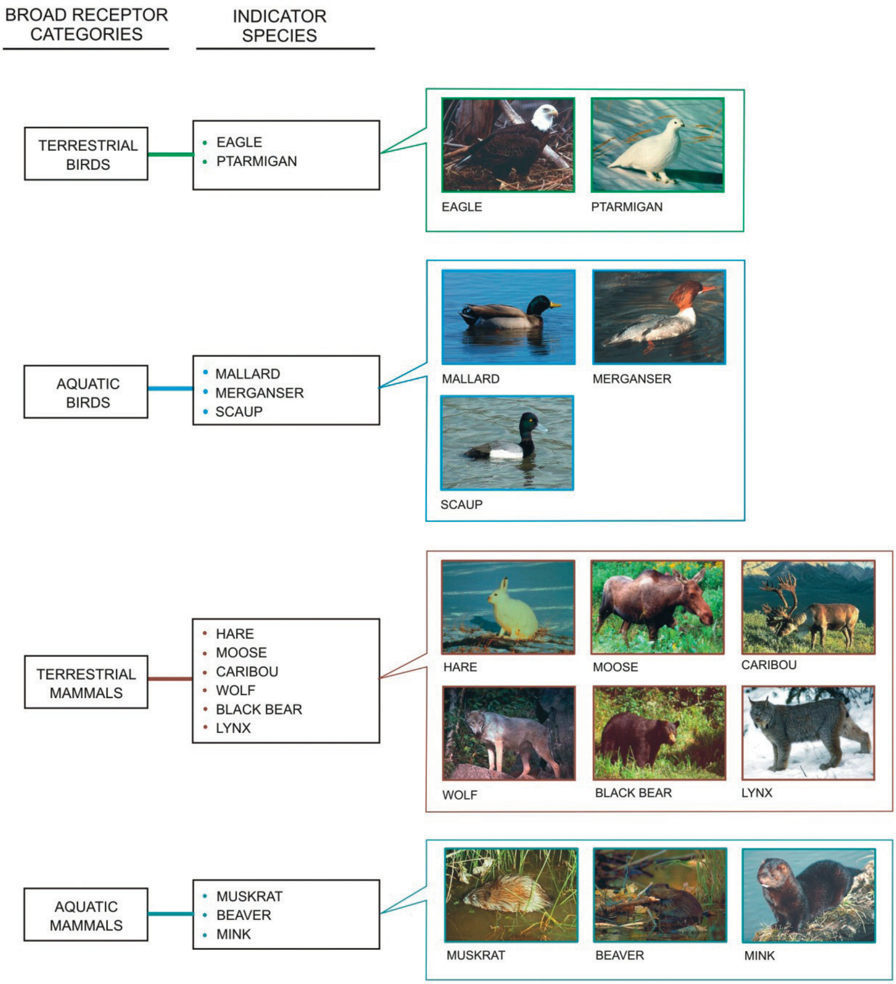

FIG. 7.2. Terrestrial receptors included in the assessment.

7.1.4. Reference dose rates

7.1.4.1. Non-human biota

The assessment of effects from exposure to radioactive constituents involves the estimation of the external gamma radiation from radionuclides in the soil or sediment as well as internally deposited radionuclides. For internal dose, it is common to take into account relative differences in the effects of alpha and beta radiation compared to external gamma radiation (annex E of Ref. [7.3]).

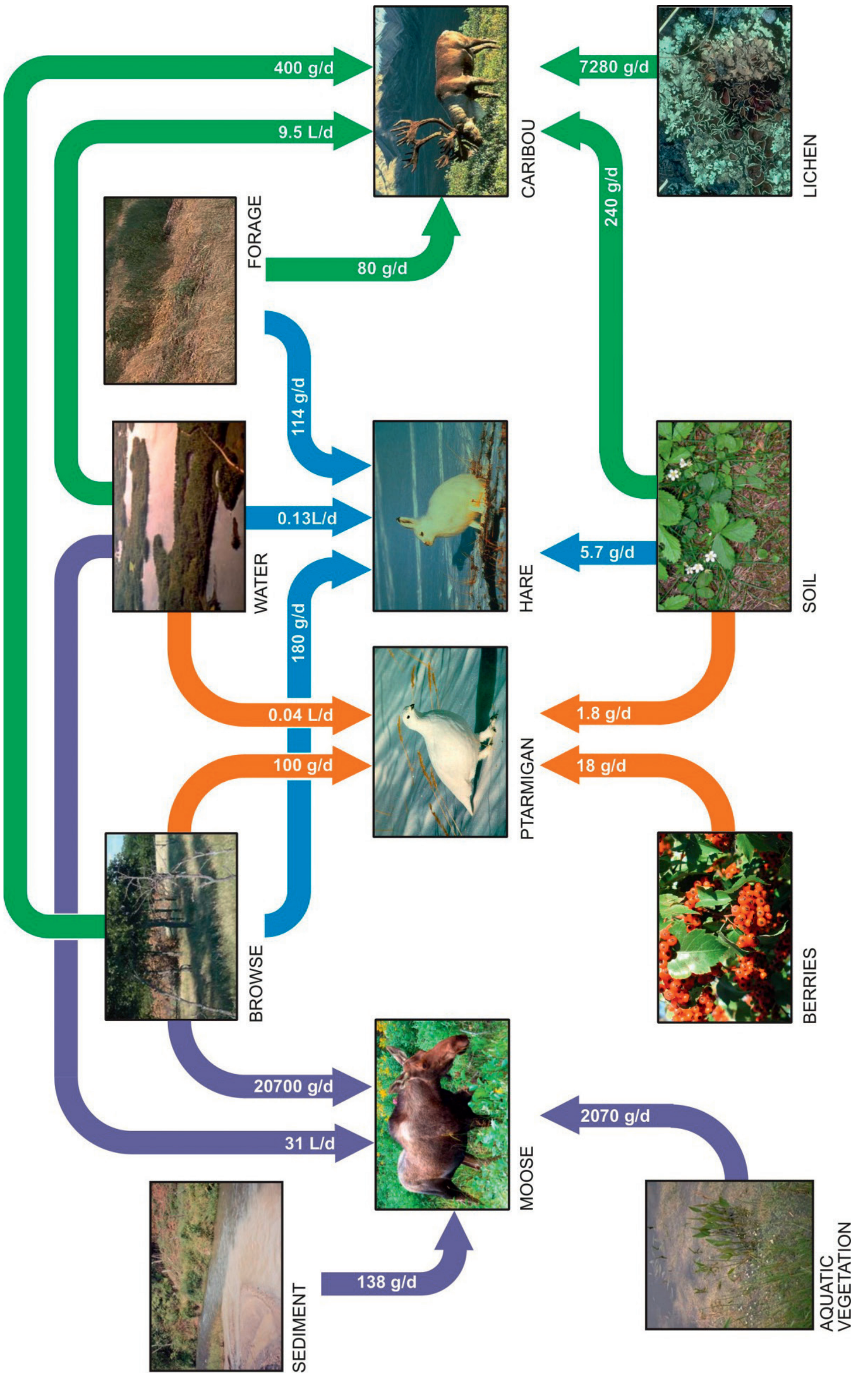

FIG. 7.3. Ecological exposure pathways for caribou, hare, moose and ptarmigan.

Radiation effects on biota depend not only on the absorbed dose, but also on the relative biological effectiveness (RBE) of the particular radiation (i.e. alpha, beta or gamma radiation). For example, alpha particles can produce observable damage at lower absorbed doses than gamma radiation. In this assessment, the terms RBE and 'radiation weighting factor' or 'ecodosimetric weighting factor' etc., are used interchangeably. The Rabbit Lake study assumed a nominal RBE of 10 to illustrate the effect of alpha RBE (based on a review by Chambers et al.) and an upper value of 40 based on a Canadian study [7.4].

A level of 1 mGy/d is generally used as an acceptable level for terrestrial biota (e.g. Ref. [7.5]). The Canadian Nuclear Safety Commission (CNSC) provided a dose rate guideline of 3 mGy/d as an appropriate level for small mammals and terrestrial plants [7.4, 7.6]. This level is based on reproductive endpoints for small mammals. In the absence of data for avian species, the CNSC suggest that the dose limit for small mammals will ideally also apply. Thus, dose limits of 1 mGy/d and 3 mGy/d were selected for the assessment of impacts on terrestrial biota.

7.1.4.2. Humans

Assessment of radiation exposures to members of the public is commonly based on the estimation of the incremental effects of the project or site. Such assessments consider the radiation dose received from direct exposure to gamma radiation as well as the dose received from ingestion of radionuclides. The human receptor model converts radionuclide intake by the human receptors from the various pathways into a dose.[1] Potential effects from radiation were compared to an incremental dose limit of 1000 μSv/y(1 mSv/y) recommended by the CNSC for the protection of members of the public.

7.1.5. Transport and fate

Environmental media concentrations were estimated using atmospheric transport modelling, aquatic transport modelling and a pathways model (details of which can be found in [7.1]). These models are based on those commonly

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[1] The dose conversion factors (DCFs) used in the assessment are those recommended by the International Commission on Radiological Protection (ICRP), [7.7].

employed in estimating environmental concentrations, such as those derived by IAEA or NCRP. A SENES model (INTAKE), which comprises an aquatic dispersion model and a pathways model, was used for this assessment. The SENES models which have been applied and tested on several other uranium mining projects in northern Saskatchewan were used to simulate constituent transport and evaluate exposures to ecological species and humans. The pathways model relies on transfer factors to estimate concentrations in environmental media. The model assumes that the biota is in equilibrium with the surrounding environment. Site-specific data were used where possible, as discussed below, augmented by values available in the literature.

7.1.6. Exposure

The pathways model is an equilibrium model and relies on concentration ratios or transfer factors to estimate concentrations in environmental media. Site specific data were used to derive transfer factors where possible, including fish, aquatic plants and benthic invertebrates, augmented by values available in the literature.

Feed to flesh transfer factors were used to estimate the concentration in wildlife. Although species specific transfer factors were used where available (e.g. Pb and Po for caribou), transfer factors were generally derived from generic transfer factors for beef and poultry. To obtain a more appropriate transfer factor, allometric scaling was used with a relationship of −0.75. This approach is consistent with that taken by others [7.8, 7.9].

7.1.7. Ecological Risks

Potential toxic effects of constituents can be measured at different levels of biological and ecological organization. For radionuclides, the total dose rate received by an ecological receptor was divided by the selected dose rate guideline to calculate a screening index value, as shown in Eq. (7.1).

$$\text{Screening index} = \frac{\text{Dose rate}}{\text{Dose rate guideline}} \tag{7.1}$$

To take into account the uncertainties including the estimates of constituent loadings to local watersheds, estimates of atmospheric emissions, estimates of exposure concentrations in various media (soil, terrestrial vegetation, fish, etc.), transfer factors and diets of receptors, the assessment was carried out within a probabilistic modelling framework. Probability distribution functions were assigned to key parameters and the model outputs (predictions) were processed to obtain summary statistics for presentation purposes. Screening index values for all species were estimated for the mean and 95th percentile predicted constituent concentrations in water or the mean and 95th percentile predicted total intakes or doses.

Spatial considerations were taken into account based on the home range of the selected receptors. For example, animals with a relatively small home range (beaver, mallard, merganser, mink, muskrat, scaup, ptarmigan and hare) were assessed at several discreet locations. Caribou and wolf, due to their large home ranges and the potential importance of airborne pathways, were assessed on a spatial scale consistent with the modelled Rabbit Lake Mill airshed. Bear, eagle, lynx and moose were assessed over the entire Horseshoe Creek watershed. Temporal variations were addressed by considering several different periods which span the entire life of the project (development and operation) and the decommissioned period.

Table 7.1 provides the detailed results of the radioactive dose assessment for all receptors assessed for screening index values based on the mean and 95th percentile dose estimates for an RBE of 10 for the maximum time period. This table shows that the eagle, mallard, merganser and scaup are the most radiologically exposed terrestrial animals. At an RBE of 10 with the expected (mean) doses in Horseshoe Pond, no SI values are above 1. However, at the upper bound dose, the mallard and scaup surpass the benchmark. Predicted doses are currently at their highest and are a result of pre-existing conditions. These doses are predicted to decrease in the near future due to improvements to the effluent treatment plant. Table 7.2 provides a summary of the contribution ^{226}Ra made to the total estimated dose.

In summary, while potential adverse effects are predicted for upper bound exposures for waterfowl, these effects will be short term and spatially confined and thus the results of the terrestrial assessment for radionuclides predicted no potential for significant adverse effects in non-human biota in Horseshoe Creek and Hidden Bay.

TABLE 7.1. SUMMARY OF SCREENING INDEX VALUES FOR RADIOLOGICAL DOSES TO ECOLOGICAL RECEPTORS

Receptor	Location	Screening index values	
		Mean	95th Percentile
Bear	Watershed	<0.001	0.002
Caribou	Airshed	0.002	0.004
Eagle	Watershed	0.082	0.30
Lynx	Watershed	<0.001	<0.001
Moose	Watershed	0.006	0.02
Wolf	Airshed	<0.001	<0.001
Hare	Close to site	<0.001	<0.001
Grouse	Close to site	0.003	0.007
Beaver	Horseshoe Pond — close to discharge	0.003	0.012
Beaver	Downstream	0.002	0.009
Mallard	Horseshoe Pond — close to discharge	0.21	0.77
Mallard	Downstream	0.16	0.55
Merganser	Horseshoe Pond — close to discharge	0.078	0.29
Merganser	Downstream	0.075	0.28
Mink	Horseshoe Pond — close to discharge	0.019	0.061
Mink	Downstream	0.016	0.053
Muskrat	Horseshoe Pond — close to discharge	0.044	0.16

TABLE 7.1. SUMMARY OF SCREENING INDEX VALUES FOR RADIOLOGICAL DOSES TO ECOLOGICAL RECEPTORS (cont.)

Receptor	Location	Screening index values	
		Mean	95th Percentile
Muskrat	Downstream	0.032	0.12
Scaup	Horseshoe Pond — close to discharge	0.43	1.5
Scaup	Downstream	0.38	1.3

Note: Results presented are for the maximum year, based on an RBE of 10 and compared to a benchmark of 1 mGy/d.

Shaded values indicated screening index values above the accepted level.

For all receptors except mallard, merganser and scaup, SI values compared to 1. For the migratory birds the screening index is compared to 0.5 as only half of exposure is accounted for in assessment.

TABLE 7.2. CONTRIBUTION OF RADIUM-226 TO DOSE ESTIMATES OF ECOLOGICAL RECEPTORS

	Total dose (mGy/d)	Contribution of Ra-226 to total
Reindeer	1.5×10^{-3}	16%
Elk	6.0×10^{-3}	<5%
Hare	1.8×10^{-4}	38%
Grouse	2.6×10^{-3}	5%
Beaver	2.9×10^{-3}	55%
Mallard	2.0×10^{-1}	<5%
Scaup	4.3×10^{-1}	<5%
Merganser	7.8×10^{-2}	<5%
Muskrat	4.4×10^{-2}	34%

TABLE 7.2. CONTRIBUTION OF RADIUM-226 TO DOSE ESTIMATES OF ECOLOGICAL RECEPTORS (cont.)

	Total dose (mGy/d)	Contribution of Ra-226 to total
Bear	6.0×10^{-4}	10%
Wolf	1.4×10^{-4}	18%
Eagle	8.2×10^{-2}	<5%
Mink	1.9×10^{-2}	6%
Lynx	1.2×10^{-5}	36%

Note: Based on mean 2010 dose estimate in Horseshoe Creek watershed.

7.1.8. Doses to humans

The air and water emissions from the Rabbit Lake facility were used in an exposure pathways analysis to predict intakes and doses to human receptors in the study area. The incremental annual radiation doses resulting from Rabbit Lake operational activities for the selected receptors are summarized in Table 7.3. The highest predicted incremental dose is 245 μSv/a for a non-nuclear worker at Rabbit Lake (e.g. for the camp cook). The maximum incremental radiation dose for a member of the public off-site is estimated at 60 μSv/a for a child resident in the Wollaston Lake community. The percentage of the dose due to intake of ^{226}Ra is also shown in the table and is typically less than 10% of the total. Dose by pathway and receptor is shown in Fig. 7.4.

Caribou meat, which is typically harvested outside the assessment area, constitutes a significant portion of meat consumed by people in this area. Exposure to naturally occurring radiation from eating caribou meat has been estimated, using the Hatchet Lake Band dietary survey [7.2] as a basis. Radionuclide concentrations measured in 15 caribou harvested from four natural sites in northern Saskatchewan [7.10] were used to characterize background radionuclide concentrations in caribou meat. The use of these background concentrations resulted in a dose estimate of about 1800 μSv/a for an adult and 2600 mSv/ a for a child, which is not related to project effects. It is noted that the predicted incremental dose from the facility is a small fraction of the dose received from naturally occurring radiation associated with eating caribou meat.

Doses are well below the recommended incremental dose limit of 1000 μSv/a, and well within the range of variability of radiation dose from natural sources.

Overall, the incremental dose from the project is so low that no impacts are expected from exposure to radiation.

TABLE 7.3. SUMMARY OF INCREMENTAL ANNUAL RADIATION DOSE RELATED TO RABBIT LAKE OPERATIONAL ACTIVITIES

Human receptor	Description/location	Average incremental radiation dose related to rabbit lake operational activities (μSv/a)[a]	% contribution due to ^{226}Ra
1a	Adult Wollaston Lake resident	22	2%
1c	Child Wollaston Lake resident	60	1%
2a	Adult Wollaston Lake Lodge operator	10	2%
2c	Child of Wollaston Lake Lodge operator	34	1%
3	Adult Wollaston Lake trapper	20	3%
4	Rabbit Lake camp worker	245	7%
5	Jeb camp worker	6	4%
6	Points North worker	3	3%
7	Adult Parks Lake cabin occupant	13	6%
8	Adult Eagle Point cabin occupant	5	58%

Note: CNSC recommended allowable incremental dose for the protection of members of the public is 1000 μSv/a.

[a] Incremental dose estimates provided for the year 2010 for all receptors except the adult occupants of the cabins on Parks Lake and at Eagle Point, which are provided for the year 2030.

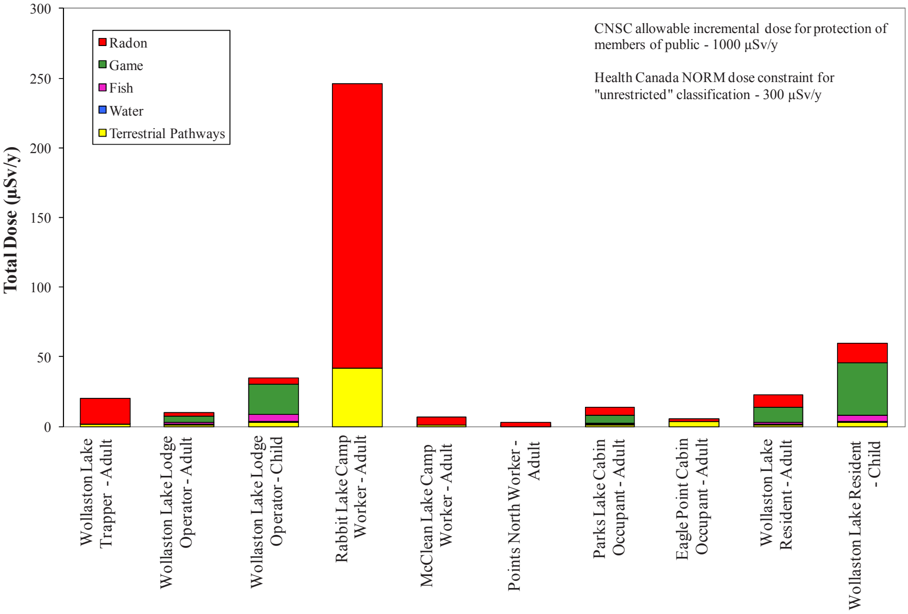

FIG. 7.4. Total radiation dose for human receptors.

7.2. RADIUM EXTRACTION PLANT OLEN

7.2.1. Background

The discovery of U containing ores in Katanga (former Belgian Congo) in 1915 led to the development of the Ra industry in Olen, Belgium [7.11, 7.12]. These ores were extremely rich in U minerals (up to 50% uraninite) and associated minerals such as Co-Ni sulphides and Pb and Mo minerals, among many others. In 1921, the first ore arrived in Belgium and in 1922, Ra production began in a factory in Olen, where the non-ferrous metals copper and cobalt were also extracted. The production continued until the mid 1960s. During that time, the company Metallurgie Hoboken-Overpelt at Olen, now part of the Umicore group, was one of the most important Ra extraction plants and contributed significantly to the widespread use of Ra in medical and industrial applications. Half of the total amount of Ra produced worldwide, estimated to be about 4.5 kg, was produced at the Olen facility.

With the development of nuclear reactors and particle accelerators after the Second World War, cheaper and more efficient radionuclides became available and interest in Ra decreased. As a result, Ra extraction in Olen was halted in

1969 and the decommissioning and dismantling of the industrial installations was completed in 1983.

The industrial activities of the Ra extraction plant have resulted in a variety of radioactive wastes, including mill tailings and dismantling and decontamination materials, which were stored in various disposal sites in the vicinity of the factory, and in non-negligible environmental contamination of the surroundings.

By chance, it was discovered in the late 1950s that the surroundings of the plant showed enhanced Ra concentrations. In the 1960s, a series of measurement campaigns was launched to get a general idea of the extent of the contamination [7.13]. Recurring media coverage in 1989 of some high (localized) contaminations in the village of Sint-Jozef, near Olen, made the federal authorities realize that the available data were insufficient for an adequate radiological impact assessment in the context of the upcoming more stringent radiation protection approach. Since then, more detailed radiological studies of the environmental contamination and evaluation of potential population impact were performed [7.12, 7.14–7.18].

The radiological studies consisted of gamma surveys carried out on the Bankloop brook and the dumping sites (river banks, inundation zones, bed sediment and water). Radon exposure in the dwellings of Sint-Jozef, the village surrounding the factory, and in open air above the dumping grounds was evaluated. Ra in airborne dust, surface water, groundwater, in the food chain and in the milk teeth of children was monitored [7.14].

The current radiological impact of the historical activities of the Ra extraction plant does not require urgent countermeasures, but the radiological impact may become important if new uses for these terrains are considered, such as the integration of the contaminated sites into residential areas, mainly because of indoor radon risk.

Umicore and the concerned authorities have been working together to define possible remediation strategies taking into account all relevant aspects (radiological evaluation, chemical and toxicological hazards, cost, public acceptance, public concern, etc.). A new Ra disposal facility has been built in Olen to incorporate a large part of the scattered contamination.

7.2.2. Overview of the environmental contamination

The Ra contamination of the surroundings of the Ra extraction plant was discovered in the late 1950s when the authorities located the Belgian Nuclear Research Centre (SCK•CEN) in the same region. The environmental survey that was required for the authorization for discharging liquid effluents from the laboratories revealed abnormal ^{226}Ra levels in some of the small rivers. It then became clear that the water and the sediments of the river Kleine Nete and the brook Bankloop were contaminated through the liquid effluents from the Ra plant in Olen. The banks of the Bankloop brook were also contaminated because the brook was dredged regularly and the sediments that were removed were placed on the banks. The contamination of the environment was made possible by the absence of adequate regulations and control of the discharge of radioactive effluents.

Radioactively contaminated liquid effluents were discharged into the Bankloop, which transported the Ra containing effluents to the Kleine Nete. The Bankloop is approximately 1800 m long from the fence of the factory to the mouth into the Kleine Nete (see Figure 18 [7.19]). The first 600 m of the brook up to the canal flows through the town centre, past the municipal school, the church and under the churchyard. Then the Bankloop flows through a predominantly agricultural area. The final 400 m of the course just before its confluence with the Kleine Nete is marshy and frequently flooded during wintertime.

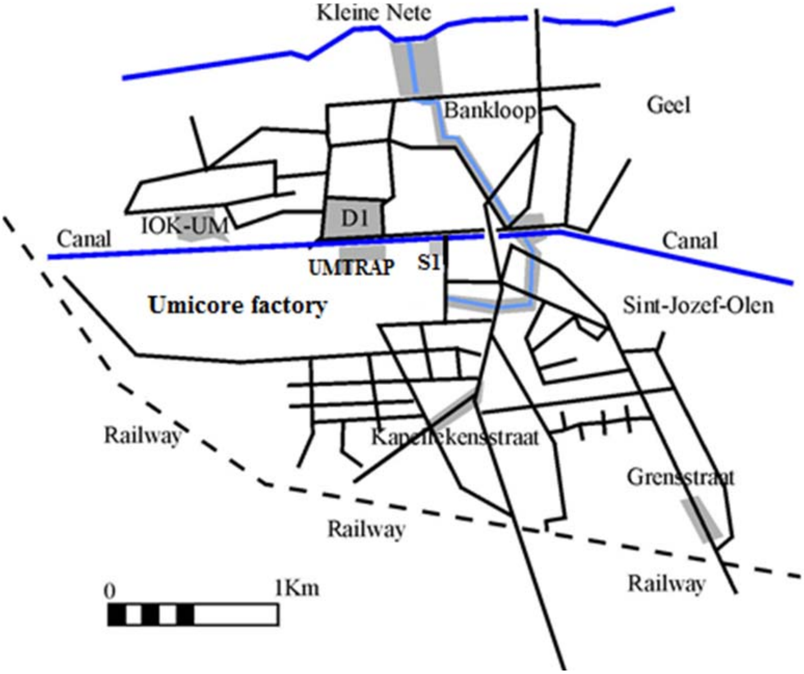

FIG. 7.5. Areas with enhanced Ra concentrations from past disposal activities or caused by liquid discharges into the Bankloop are indicated in grey. This represents the historical contamination until the 1990s. Since then, several cleanup operations have been carried out. The Umicore factory is the former Ra extraction plant [7.19].

Several measurement campaigns have been carried out to evaluate the extent of the environmental contamination, the dispersion throughout the food chain and other human exposure pathways.

The Ra contamination of the Bankloop was mapped from the fence of the Umicore factory to its confluence with the Kleine Nete [7.14]. In the first 1400 m downstream of the discharge point, the enhanced dose rates were mostly confined to a narrow strip of 5 to 10 m wide on one or both banks of the brook, caused by regular dredging of the sediment. Depth profiles have shown that the most contaminated layer is often at a shallow depth (between 20 and 40 cm) [7.14, 7.16]. This demonstrates the relatively low mobility of Ra in soil.

Enhanced dose rates were also observed in the former flooding zones of the Bankloop, which were transformed in the beginning of the 1960s into farmland with pastures and cultivation, mostly of maize for feeding cows. Soil Ra concentrations were derived from the dose rate measurements and used to perform dose calculations.

About 16 ha of farmland is contaminated up to 1 m deep with widely varying soil Ra concentrations. Based on these results, the area was divided into 4 subplots ranging from minor contaminatation (average soil Ra concentration of 40 Bq/kg) to severely contaminated (average soil Ra concentration of 1040 Bq/kg) as shown in Fig. 7.6. Dose assessments have shown that restrictions have to be placed on the type of farming on the three most contaminated plots (average soil concentration of 140 Bq/kg or more) [7.20].

Other places in the village of Sint-Jozef and in the neighbouring city of Geel also became contaminated because Ra contaminated waste material was used as paving materials. Nine or ten stretches of road and several isolated points were identified during the different gamma surveys. The two most contaminated roads, namely, the Kapellekensstraat and the Grensstraat, were remediated on behalf of the municipal authorities in the late 1990s and the contaminated materials were removed to the D1 dump.

During the extensive measurement campaign of 1991–1992, the ^{226}Ra concentrations in aerosols, food chain samples (including grass, milk, maize, chicken eggs, leek, celery and scorzonera) and in the milk teeth of children were also measured [7.14]. The measurements showed the concentrations in aerosols to be radiologically insignificant and the internal contamination from local foodstuffs to be limited to a few tens of μSv/a. The dose due to ingestion of local food products is limited because at present no crops for direct human consumption are grown on the contaminated farmland.

In order to examine the internal contamination of children in Sint-Jozef, the milk teeth of children were collected in a municipal school, close to the former Ra plant (176 teeth from 40 children) and their ^{226}Ra concentration measured.

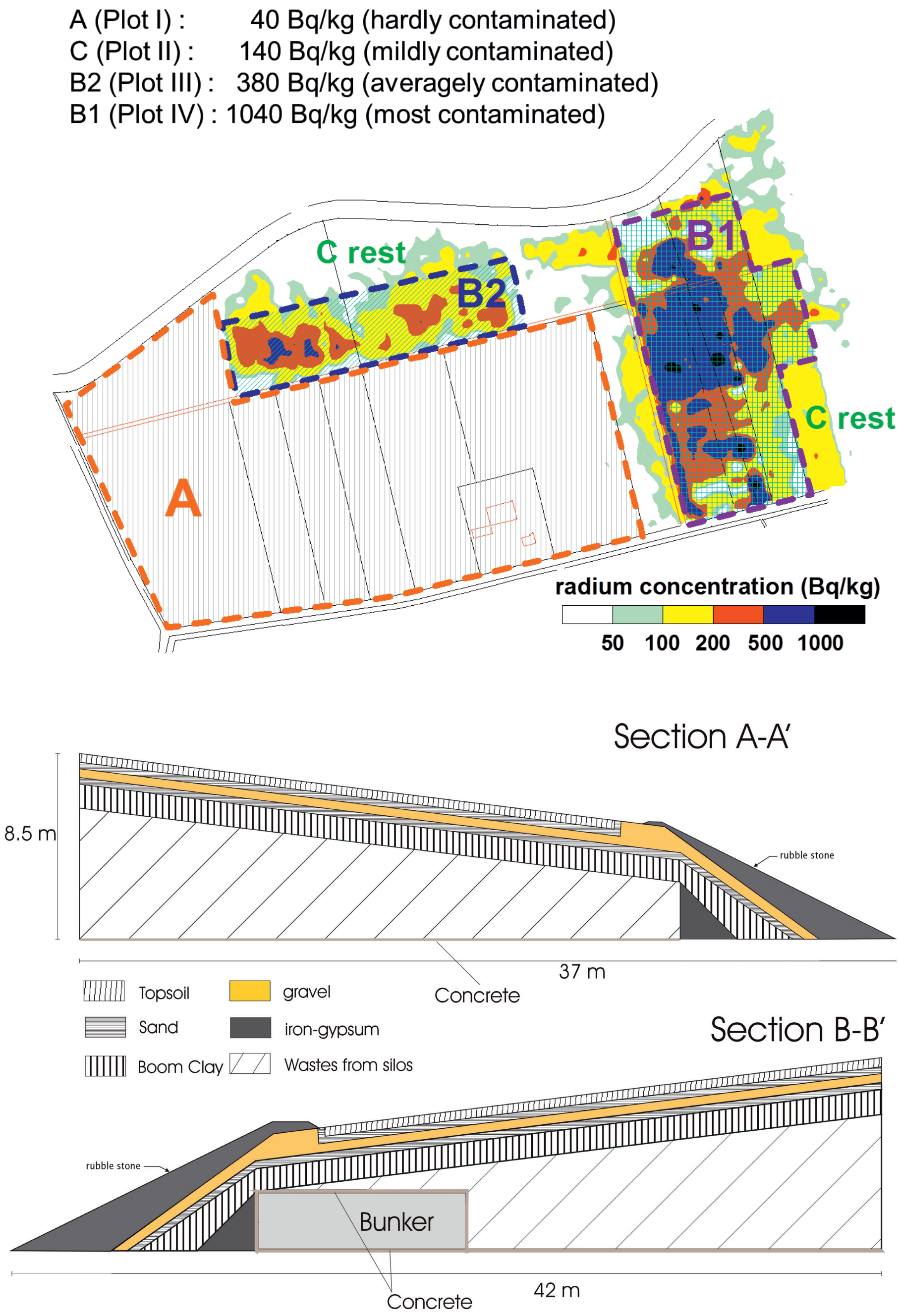

FIG. 7.6. Overview of the repartitioning of the contaminated farmland into four subplots based on the soil Ra concentration and practical restrictions.

The influence from the Ra contamination at the site was shown to be very small [7.14].

For many years, most contaminated areas have been left untouched, because not only radiological contamination but also chemical pollution by heavy metals had to be dealt with and those matters are handled by different authorities with different jurisdictions for which different regulatory requirements had to be taken into account.

Finally, in the years 2006–2009, the river bed and banks of the Bankloop were remediated by the authorities concerned and the excavated contaminated soil and sediment is now stored in a dumping site, the so-called Bankloop dumping site described below.

7.2.3. Overview of the legacy sites

There are several legacies in the vicinity of the Ra production factory and most sites have still to be remediated. An overview of the different waste disposal sites is given in Fig. 7.7.

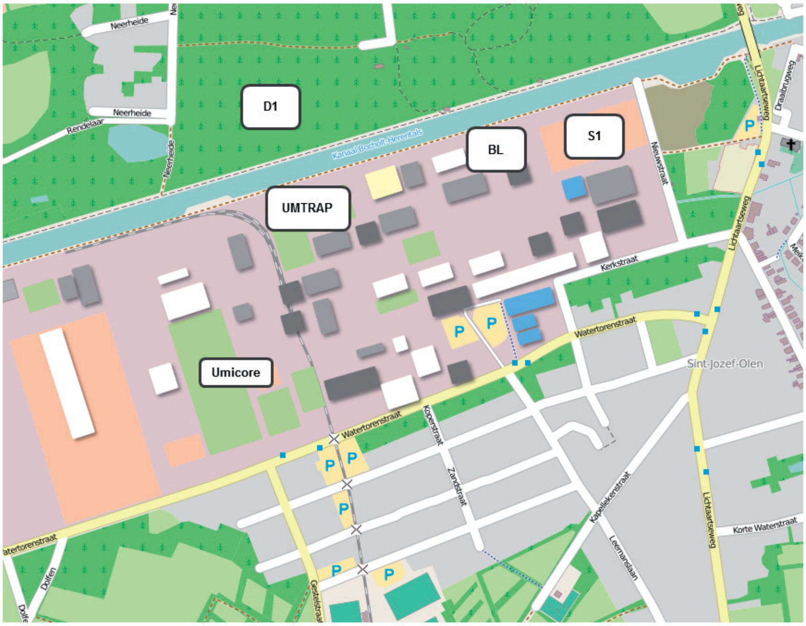

FIG. 7.7. View of the Olen site with location of D1 and S1 landfills and the UMTRAP and Bankloop (BL) storage facilities. (Map copyright held by www.OpenStreetMap.org contributors.)

7.2.4. The UMTRAP facility

UMTRAP (Uranium Mill Tailings Remedial Action Plan) is a licensed storage facility on the site of the industrial plant at Olen containing the most radioactive Ra bearing waste, including [7.21, 7.22];

- 2000 t of tailings with a total of 700 g ^{226}Ra and ^{226}Ra activity concentrations of up to 30 000 Bq/g;
- 4000 t of residues containing ^{226}Ra, with a total of 110 g ^{226}Ra and a ^{226}Ra activity concentration of up to 7500 Bq/g;
- Ra needles (around 200 g ^{226}Ra);
- 60000 t of contaminated soil and materials used for dismantling with an average Ra concentration of 15 Bq/g.

The surface repository was built in the mid 1950s and consisted of a set of concrete bunkers for high activity waste and open silos for low activity waste. In the mid 1980s, the repository was remediated and re-engineered for the final disposal of radioactive waste (Fig. 7.8). Because the quality of the 30 year old concrete bunkers was unknown, they were reinforced by an additional concrete cover. After reinforcement of the bunkers, concrete wall liners were built

FIG. 7.8. View of the L-shaped UMTRAP facility at Union Minière, Olen.

surrounding the bunkers and open silos. In addition, the entire site, approximately 13 600 m^2 in area including bunkers and silos, was isolated from the environment by means of a 2.5 m thick multi-layer cover containing a 1.1 m thick clay cap, so as to comply with the radiological criteria for a radioactive waste disposal facility (Fig. 7.9). The thickness of the concrete bottom of the disposal system was also increased.

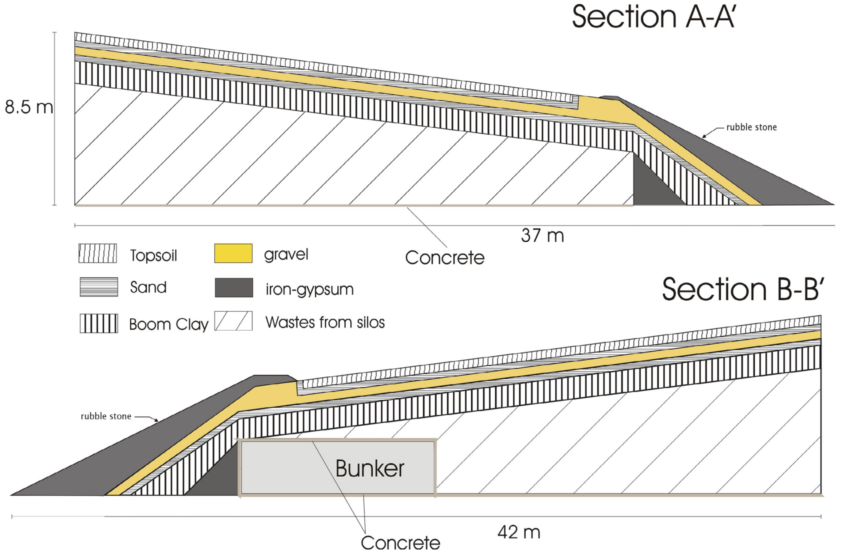

FIG. 7.9. Cross-sectional view of one half of the multilayer cover.

Owing to the Ra processing activities which took place at the Olen site for more than half a century, the soil beneath and in the vicinity of the disposal site has become contaminated with Ra, U, Pb, As, etc. Depth profiles of 2.5 m [7.23] and 8.5 m [7.21] were taken and the Ra concentrations were monitored. The results revealed that the Ra concentration in the upper few metres is approximately 5 times higher than the local mean background concentration of 0.013 Bq/g. The total U concentrations of the 8.5 m deep soil profiles were also measured and varied between 0.2 and 1 Bq/g while up to 10 Bq/L U was found in the pore water. Since Pb and As were present in the waste, it was investigated whether they were also present in the soil profiles. Measurements indicated that the soil in the near vicinity of the repository was contaminated with As, but not with Pb. It is, however, not clear whether the elevated As concentration is due to historical contamination from the processing activities. Other contaminants were not investigated.

Assessment of the long term safety of the repository was carried out in 2001 [7.21, 7.24]. The most important exposure pathway by which the contaminants can reach humans was considered to be via leaching to groundwater and the use of groundwater for drinking and irrigation purposes. A schematic overview of such a pathway is seen in Fig. 7.10.

Results from the calculations showed that leaching from the waste forms containing the highest concentration in Ra and U (i.e. various U mill tailings and Ra sources and needles) does not lead to unacceptable Ra and U concentrations in the groundwater for the first 1000 years and therefore only causes negligible doses to humans. Also, for the conventional contaminants such as Pb, Ni and Mo present in the U mill tailings, the calculated concentrations in groundwater were

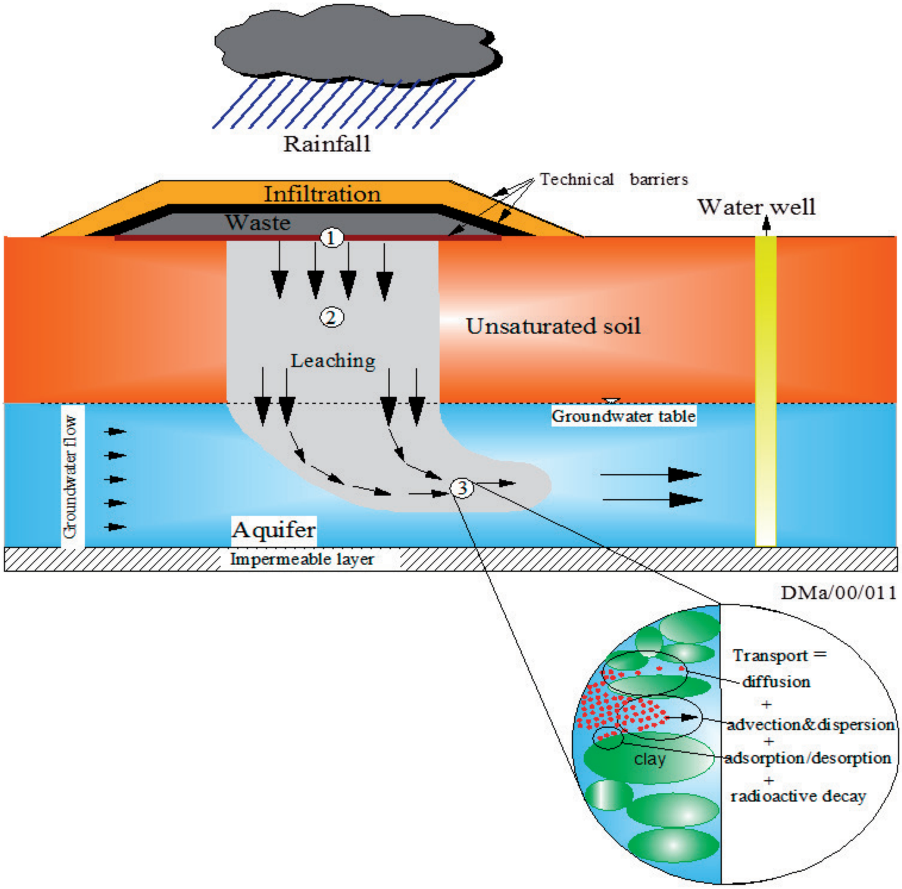

FIG. 7.10. Schematic view of the processes considered in the safety assessment calculations in case of contaminant migration from surface repository to groundwater [7.20].

below the groundwater remediation standards [7.25]. The results further showed that leaching of Ra and U present in soils covered with the multilayer barrier would only lead to non-negligible concentrations of Ra, U and heavy metals after more than 500 years.

In a preliminary scenario to assess the potential risk for humans [7.24], not only the scenario as described above with constant biosphere and gradual leaching was considered. Alternative scenarios were also identified, such as the gradual leaching scenario with changing climate, barrier degradation and human intrusion scenarios (constructions on-site, residence on-site, borehole drilling and waste retrieval). With respect to the alternative scenarios, drastic scenarios causing direct exposure of humans to the waste (primarily inadvertent human intrusion) and less drastic ones, only enhancing the release of the radionuclides into the biosphere, have been considered.

The gradual release scenario and less drastic alternative scenarios were shown to yield negligible individual doses to the representative person (less than 10 μSv/a). Only when initial degradation of the clay cap was taken into account, was a dose value of nearly 0.1 mSv/a predicted within 10 000 years. Human intrusion scenarios were predicted to yield doses exceeding 100 mSv/a, the generic reference level above which intervention is almost always justifiable [7.26]. The higher individual doses were brought about through the construction scenario, consisting of the widening of an existing canal along the site and through the residence scenario, consisting of the living of families in dwellings built on the mound, with respectively 120 mSv to the workers at the canal and 160–600 mSv/a to the residents. The major exposure pathways corresponding with these scenarios were external irradiation by ^{226}Ra and daughters, and inhalation of radon exhaled from the waste into the dwelling, repectively. In the case of exceeding the 100 mSv/a level, the ICRP recommends efforts to reduce the probability of human intrusion or to limit its consequences. However, the corresponding scenarios have a low probability of occurrence, making it likely that a total radiological risk equivalent with an annual dose of 10 mSv/a is not attained, and that intervention is not justifiable.

7.2.5. The licensed Bankloop storage facility

The radioactive wastes resulting from the remediation project of the Bankloop were disposed of in the licensed Bankloop storage facility.

During Ra production, the effluents from the Ra production facility were discharged in the Bankloop brook, which led to a contamination of the sediments and, as a consequence of dredging, to a contamination of the banks of the brook. These banks were remediated in 2006–2008 but due to the limited capacity of the surface storage facility, there is still some residual contamination.

At the UMTRAP and Bankloop disposal installations, a radiological monitoring program has been implemented. The radon concentrations in the open air and concentrations in the surface waters are measured around both installations. Table 7.4 [7.27] shows the highest and lowest values measured during 2009. The values vary as a function of the location of the measurement point and the season [7.27]. If a person spent 4 hours per day on the installations, the inhalation of outdoor radon progeny would lead to a maximum dose of 0.9 mSv/a. The dose due to ingestion of 1 L of groundwater or surface water per day is more than a factor of 20 lower.

TABLE 7.4. LOWEST AND HIGHEST CONCENTRATIONS MEASURED FOR RADON IN AIR AND RADIUM IN SURFACE WATER, GROUNDWATER AND PERCOLATE WATER AT UMTRAP AND THE BANKLOOP STORAGE FACILITY

	UMTRAP			Bankloop storage facility		
	Monitoring points (*n*)	Min.	Max.	Monitoring points (*n*)	Min.	Max.
Concentration ^{222}Rn, open air (Bq/m)	3	56	105	6	24[a]	199
Concentration ^{226}Ra, surface water (mBq/L)	2	13.3	20.9	2	8.2	240
Concentration ^{226}Ra, groundwater (mBq/L)	4	6.2	19.5	4	13	380
Concentration ^{226}Ra, percolate (mBq/L)	0	-	-	1	175	398

[a] Background level

7.2.6. The D1 landfill

The D1 dump is located along a canal (Herentals Bocholt canal). It covers an area of 9 ha and contains mixed Ra and chemical wastes, i.e. residues from Ra extraction and rubble from the dismantling of buildings from the Ra facility and iron hydroxide and calcium sulphate from non-ferrous activities. The total volume of the D1 landfill is estimated at ~217 000 m^3. The Ra concentration is highly inhomogeneous with activities ranging from background values up to 0.93 Bq/kg. About 135 000 m^3 is Ra bearing material and approximately 82 000 m^3 has a negligible Ra content. The average ^{226}Ra concentration of the dump was estimated at ~20000 Bq/kg.[2] The activity of ^{238}U is ~200 Bq/kg and the activity of ^{230}Th is similar to and in some cases higher than the activity of ^{226}Ra. Thorium-232 and its daughter nuclides were not different from natural background levels. The radon concentrations in open air on and near the D1 disposal site were measured monthly for a period of one year with alpha track detectors. The locations and the annual average radon concentrations are indicated in Fig. 7.11. The yearly average radon concentration at 1.5 m above ground was 180 Bq/m³, with monthly averages of up to 500 Bq/m³. The radon concentration at 0.5 m was 2–4 times higher, indicating a high exhalation flux density. At a short distance from the D1 dump in the prevailing wind direction, an average radon concentration of 170 Bq/m³ was measured in the garden of a residential dwelling [7.12, 7.14].

Despite the sometimes dense vegetation, gamma measurements were performed every 25 m. The maximum, mean and median values of the grid measurements were 150, 2.8 and 1 µSv/h. The dose rate often varies over several orders of magnitude over distances of a few metres [7.11].

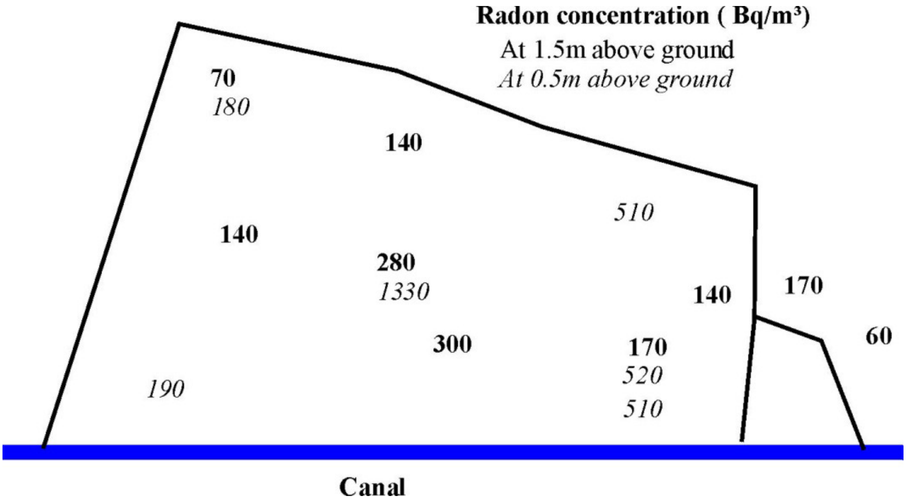

FIG. 7.11. Annual average radon concentrations (Bq/m³) at and in the vicinity of the D1 dump measured at 1.5 m above ground (bold) and at 0.5 m above ground (italics).

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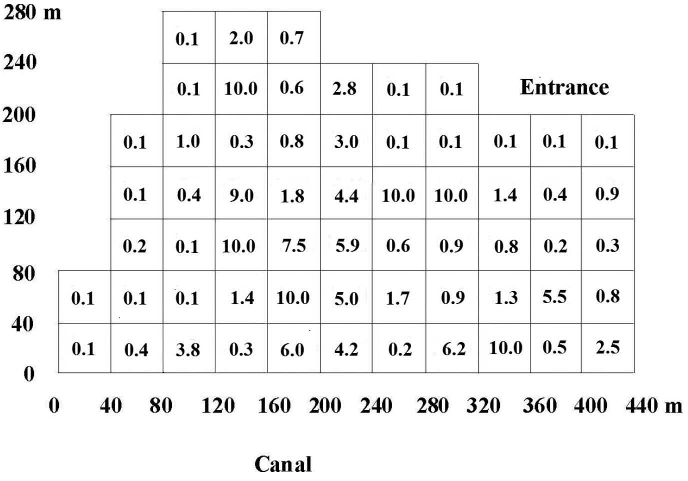
[2] Due to the highly inhomogeneous distribution, the value of the average may vary according to the way it is calculated.

In addition, the 3 m depth profile of the Ra contamination of the D1 dump was measured every 40 m [7.15]. The dose rate profile was measured by lowering a NaI detector into the borehole. The maximum dose rates of the 61 borings (one borehole per square) in the waste at 50 to 100 cm below the ground's surface are shown in Fig. 7.12.

Samples of surface waters in the vicinity of the dumping ground D1 were taken and the ^{226}Ra content was measured. The observed ^{226}Ra concentrations of those waters were about 0.03 Bq/L. The groundwater below the dumping grounds was also sampled and the samples showed the migration of ^{226}Ra to the groundwater to be insignificant (^{226}Ra concentrations of maximum 0.02 Bq/L) [7.14]. The EU drinking water directive [7.28] gives an annual total indicative dose of 0.1 mSv/a as an indicator parameter (for monitoring and further action purposes) for radiation in drinking water. For a member of the target group, i.e. infants younger than 1 year, this limit results in a maximum concentration of 0.09 Bq/L ^{226}Ra. The concentrations observed in the vicinity of the dumping site are well below this limit.

Different possible remediation options for the D1 dumpsite were evaluated in 1996 [7.17]. The study investigated the human dose impact of different scenarios concerning the future use of the dumping site before (current situation) and after implementation of one of the possible remedial actions. The study considered the gradual leaching scenario with no major changes in the use of the dumpsite and of the surrounding areas and two intrusion scenarios on the



		0.1	2.0	0.7						
		0.1	10.0	0.6	2.8	0.1	0.1	Entrance		
	0.1	1.0	0.3	0.8	3.0	0.1	0.1	0.1	0.1	0.1
	0.1	0.4	9.0	1.8	4.4	10.0	10.0	1.4	0.4	0.9
	0.2	0.1	10.0	7.5	5.9	0.6	0.9	0.8	0.2	0.3
0.1	0.1	0.1	1.4	10.0	5.0	1.7	0.9	1.3	5.5	0.8
0.1	0.4	3.8	0.3	6.0	4.2	0.2	6.2	10.0	0.5	2.5

FIG. 7.12. The maximum dose rates (μSv/h) measured in the waste layer at 50–100 cm below of the D1 dump surface.

site (construction scenario and residential scenario (i.e. person living in a house built on the site)) for the current situation and for different remediation options. The main remediation options were (a) isolation of the waste material by means of a multilayer cover including a 1 m thick clay layer, (b) separation of the chemical waste from the radioactive waste and removal of the chemical waste to an industrial disposal site, and (c) relocation of the waste to a nearby area and the covering of the radioactive waste with the chemical waste.

The results showed that for the current, unremediated situation, radon is the main contributor to the dose of people living close to the site. A person who spends 20% of the year outdoors on the disposal site receives an annual radon inhalation dose of approximately 1 mSv. Doses due to gradual leaching of radionuclides from the storage facility to the groundwater (in the order of a few µSv/a) are negligible for all remediation options, while the intrusion scenarios yield doses of up to a few mSv for the construction scenario and exceeding 100 mSv/y for the residence scenario.

Access to the waste disposal is now prevented by a fence and reasonable efforts will ideally be made to reduce the probability of human intrusion or to limit its consequences.

A global restoration plan was developed in 2001 based on the radiological study of 1996 [7.18], but has not yet been implemented.

7.2.7. The S1 landfill

The S1 landfill is also located inside the factory premises. It contains mainly residues (iron hydroxide and calcium sulphate) from the cobalt production facility and Ra contaminated dredging sludge from the nearby Bankloop river. The total volume of the S1 landfill is estimated at ~207 000 m^3. Dose rate measurements have been performed in boreholes showing that contaminated material is present essentially in a band at 6–8 m depth (8–10 m above the surrounding ground level) in the eastern part of the deposit. The average ^{226}Ra activity concentration in this contaminated band has been evaluated to be ~10 Bq/g (1 Bq/g if averaged over the whole volume of the landfill). In some samples, activity concentrations of ^{238}U of up to 2 Bq/g (and 2.6 Bq/g for ^{230}Th) have been measured. Activity concentration of these two nuclides in the other samples was much lower.

7.2.8. The IOK-UM disposal site

The present municipal (IOK) and industrial (UM) disposal site are located at a former dumping ground for ^{226}Ra contaminated waste. The radioactively contaminated waste is buried under 15 m of non-radioactive waste.

7.2.9. Concluding remarks

The various measurement campaigns have shown that the present contamination in the vicinity of the Ra extraction plant poses no threat to public health. Direct exposure to the radioactive disposal sites is prevented and indirect exposure via groundwater dispersion is negligible. However, unrestricted land use of the contaminated farmland is not recommended because the use of the contaminated areas for cultivation of food crops or as residence area could lead to non-negligible doses.

7.3. RADIUM-228 AS A BASIN SCALE INTEGRATOR OF SGD TO THE ATLANTIC OCEAN

Over the last decade, SGD has become recognized as an important pathway for the transfer of dissolved materials between the continents and oceans. Here, SGD refers to all water, salty and fresh, which is exchanged between the land and sea at continental or island margins. This process contributes nutrients, carbon and metals to coastal waters [7.29]. However, measurement of SGD is difficult on regional and larger scales. To evaluate the overall importance of SGD, it would be advantageous to know the total flux to each ocean.

Because of their different half-lives, Ra isotopes provide information over a range of temporal and spatial scales. Radium-228, with a 5.75 year half-life, enters the upper ocean from the continents and mixes throughout surface waters. Strong gradients occur in both horizontal and vertical dimensions because of radioactive decay (Fig. 7.13).

Twelve per cent of the total ^{228}Ra inventory in the ocean decays each year by this process ($\lambda = 0.12$/a); to maintain steady state, there must be an equivalent ^{228}Ra flux from continental margins, as ^{228}Ra released from deep-sea sediments (depths of 3000–6000 m) does not penetrate into the upper 1000 m. It is known that SGD is an important component of this ^{228}Ra input from the continental flux.

We may use these observations to develop a strategy for determining the total SGD flux to the Atlantic Ocean. First, we measure the total ^{228}Ra inventory in the upper ocean to calculate the decay loss. This provides an estimate of the flux to near surface waters from the continents, assuming the distribution is steady state. Then we evaluate other sources to the upper ocean including release from near-shore and continental shelf sediments and river input. If more ^{228}Ra is decaying than is being supplied, an additional source is required; we assume this source is SGD because no other sources are known.

The Transient Tracers in the Ocean project mapped ^{228}Ra and ^{226}Ra distributions in the Atlantic Ocean during 1981–1989. These data have been used

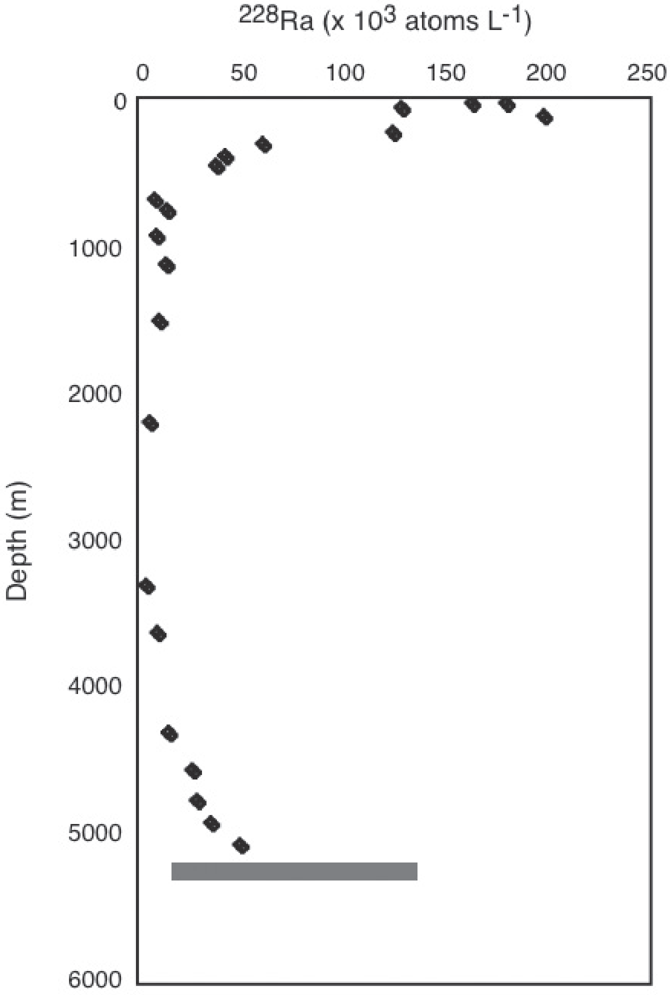


FIG. 7.13. Typical depth profile of ^{228}Ra (×10^3 atoms/L) in the Atlantic Ocean. The grey bar indicates the seabed. Note that significant concentrations occur in near surface and near bottom waters, but not in waters between 1000 and 4000 m depth. The 5.75 year half-life limits the downward and upward penetration from the source regions.

to determine the inventory of ^{228}Ra in the upper Atlantic [7.30]. Over 150 stations had at least 8 samples collected in depth profiles in the upper 1000 m, allowing a comprehensive estimate of the ^{228}Ra inventory in the upper Atlantic.

The ^{228}Ra inventory (atoms/m^2) was evaluated by linear interpolation between samples 0–1000 m deep at each station. Between 1000 and 2000 m depth, ^{228}Ra was below detection with respect to blank (Fig. 7.13). To calculate the total inventory, the stations were grouped into 15° × 15° boxes; all profiles in each box were used to calculate a bin average (Fig. 7.14). These bin averages were used to calculate a grand average. The grand average (3.0×10^{10} atoms/m^2) was multiplied by the surface area of the Atlantic to calculate the upper Atlantic inventory of 2.9×10^{24} atoms. Twelve per cent of this inventory (3.48×10^{23} atoms) decays each year. The Ra residence time with respect to scavenging from the surface ocean is ~500 years [7.31]; the ^{228}Ra residence time with respect to decay is 8.3 years. Therefore, 1.6% of the ^{228}Ra inventory is lost by scavenging and 98.4% is lost by decay, for a total loss of 3.5×10^{23} atoms/a (1.3×10^{15} Bq/a).

To determine the fraction of the required flux that is due to SGD, other sources of ^{228}Ra to the ocean were evaluated [7.30]. Release from fine grained sediments contributes 37%, rivers contribute 7% and atmospheric deposition contributes <1%; the remaining 55% must come from SGD. Measurements of ^{228}Ra in coastal groundwater (mostly salty groundwater) from the Atlantic coast were used to establish an unbiased estimate of the mean concentration, 6.2×10^6 atoms/L. Dividing the SGD ^{228}Ra flux by this mean concentration revealed that the ^{228}Ra loss from the upper Atlantic requires a SGD water flux of $(2–4) \times 10^{16}$ L/a. Thus, the SGD flux is probably between 0.8 and 1.6 times the river flux of 2.4×10^{16} L/a to the Atlantic. It must be stressed that SGD is a mixture of salty and fresh water, thus, the subterranean fresh water flux is not determined. However, the concentrations of nutrients, metals and carbon are typically higher in SGD than in riverwater passing the estuary filter; therefore, we expect SGD to be more important for the input of these materials to the ocean.

The international GEOTRACES project is expected to provide new data on the distribution of ^{228}Ra in the ocean. These data will be used to test the steady state assumption for the balance of ^{228}Ra in the Atlantic and to estimate ^{228}Ra inventories in other oceans.

7.4. WISMUT ENVIRONMENTAL REHABILITATION PROJECT

7.4.1. Background

From 1946 to 1990 the then German Democratic Republic company Wismut produced 216 000 t of U and thus became the world’s third largest U producer at that time. Due to the mining of low grade ore, about 800 million t of waste rock material, radioactive sludges and overburden material were deposited at the sites. The mining and milling activities resulted in seriously affected and devastated areas of about 10 000 km^2 in Saxony and Thuringia.

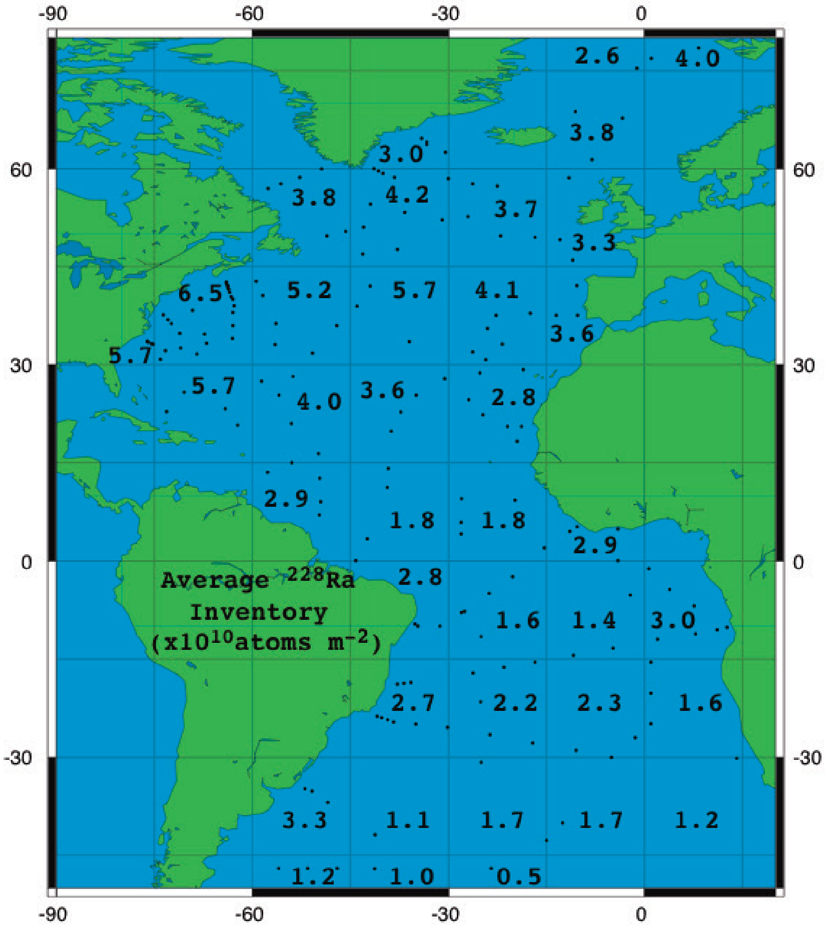


FIG. 7.14. The inventory of ^{228}*Ra (*$\times 10^{10}$ *atoms/m*^{2}*) in the upper 1000 m of the Atlantic Ocean based on data collected from 1981–1989. The points show the distribution of stations that were used to calculate* ^{228}*Ra inventories. All stations within each 15°×15° box were averaged to yield a bin average, shown as a number in each box. The bin averages were then averaged to yield a grand average for the upper Atlantic. The grand average was multiplied by the surface area of the Atlantic to estimate the total* ^{228}*Ra inventory in the upper Atlantic (adapted from Moore et al. [7.30]).*

In 1990, after German reunification, U production ceased and the German government was faced with one of its largest ecological and economic challenges, because Wismut switched at once from the production to the decommissioning phase without any preparation or preplanning. Since 1991, the national corporation Wismut GmbH has been charged with the decommissioning of the mines, mills and other facilities and with the rehabilitation of the sites. The government earmarked a total of € 6.4 billion (at the time, approx. 6.1 billion USD) to rehabilitate the U mining and milling legacy at the affected sites. The overall project includes abandonment and flooding of underground mines, relocation and covering of waste rock piles, dewatering and geochemical stabilization of tailings management facilities, demolition of structures and buildings, treatment of contaminated water, site clearance and site rehabilitation [7.32]. Table 7.5 provides an overall view of the scale of the legacies left behind. Major environmental impacts due to the legacies, as well as rehabilitation measures aimed at their mitigation, are listed in Table 7.6.

TABLE 7.5. URANIUM PRODUCTION LEGACIES IN SAXONY AND THURINGIA TO BE REHABILITATED BY WISMUT GMBH

Sites		Schlema, Pöhla	Königstein, Gittersee	Ronneburg	Seelingstädt, Crossen
Size of industrial areas		5.7 km^2	1.4 km^2	16.7 km^2	13.1 km^2
Waste rock piles	Number	22	3	16	9
	Area	3.7 km^2	0.4 km^2	6.0 km^2	5.3 km^2
	Volume	47 million m^3	4.5 million m^3	188 million m^3	72 million m^3
Tailings management facilities	Number	1	3	3	7
	Area	0.035 km^2	0.046 km^2	0.09 km^2	7.1 km^2
	Volume	0.3 million m^3	0.2 million m^3	0.25 million m^3	160 million m^3
Mines	Number	2	2	1	1
Open pits	Number	—	—	1	—
	Area			1.6 km^2	
	Volume			84 million m^3	

— = no data available

TABLE 7.6. RESIDUES, ENVIRONMENTAL IMPACTS AND KEY REHABILITATION MEASURES OF THE WISMUT PROJECT

Remaining objects/ residues	Environmental impacts / exposure pathways	Rehabilitation options
Underground mines	Groundwater contamination due to mine flooding	Controlled flooding, including surface treatment of mine water
	Settlements, mine damages	Stabilization of near surface mine workings (backfilling)
Mine dumps	Radon exhalation; external radiation; incorporation of contaminants; contamination of water bodies	Mine dump relocation (underground, off-site); rehabilitation in situ involving regrading, covering and vegetating
Worked out open pit mine, overburden dumps	Landscape devastation, groundwater impacts	Relocation of overburden dumps into worked out open pit mine, covering and vegetating
Tailings management Facilities	Radon exhalation; external radiation; incorporation of contaminants; groundwater impacts	Dry in situ rehabilitation (removal of supernatant water; sludge stabilization using deep drains; covering; treatment of supernatant, pore and seepage waters)
Contaminated structures	Use restriction	Demolition, decontamination, salvage, safe storage of contaminated materials
Contaminated plant areas	Groundwater impacts; use restriction	Area remediation (excavation / safe storage of contaminated materials, in situ soil restoration)
Rehabilitation related low level waste (e.g. water treatment residues)	Radon exhalation; external radiation	Immobilization; storage underground, in tailings pond beach areas or engineered facilities

The Wismut Rehabilitation Project has been running for 20 years. An additional 10 years will be required to bring physical remediation works to a favourable conclusion, and the subsequent stage of long term tasks (focused on water treatment and environmental monitoring) is estimated to take at least another 20 years to complete. In terms of size and remedial period required, this makes the Wismut Environmental Rehabilitation Project the largest of its kind worldwide in the field of remediating U mining and processing legacies [7.33].

7.4.2. Radium at Wismut sites

7.4.2.1. Inventory in solids

Radium is a key element in the remediation of U production legacies, with the radionuclide ^{226}Ra of particular importance as one of the decay nuclides in the ^{238}U decay chain. In solids, ^{226}Ra is encountered in a variety of specific activities, depending on the depth of technological impact. With regard to mine dumps of waste rock, the presence of a radiological equilibrium of ^{226}Ra to ^{238}U may be assumed since solely natural elution processes will have caused minor shifts in the radioactive equilibrium. In residues of chemical U ore processing (known as tailings), ^{226}Ra occurs in increased levels, as U has already been extracted from the ore, and for this reason ^{238}U is present in significantly lower specific activities than ^{226}Ra. Residues from the treatment of contaminated mine waters have the highest specific activities, and the ratios of ^{226}Ra to ^{238}U are strongly dependent on treatment technologies applied at the six individual treatment plants at Wismut. Table 7.7 provides an overview of ^{226}Ra in solids in terms of guidance values to illustrate orders of magnitude.

TABLE 7.7 RADIUM LEVELS IN URANIUM ORE MINING AND PROCESSING LEGACIES (SOLIDS) AND WATER TREATMENT PROCESS RESIDUES

Material	Volume (m^3)	specific activity $a_{Ra\text{-}226}$ (Bq/L)	Ratio $a_{Ra\text{-}226}$ / $a_{U\text{-}238}$	Inventory (Bq)	Comment/assumption
Mine dumps	3.1×10^8	0.3–1.0	approx. 1.1	2.5×10^{14}	density = 1.6 t/m^3 $a_{Ra\text{-}226}$ = 0.5 Bq/g
Tailings	1.6×10^8	1–10	approx. 20	1.2×10^{15}	density = 1.4 t/m^3 $a_{Ra\text{-}226}$ = 5 Bq/g
Water treatment residues annually	28 000	2–50	Site specific, varying greatly due to differing water treatment technologies		

7.4.2.2. Radium in mining influenced waters

Water concentrations of ^{226}Ra show significant variations at the various sites under remediation by Wismut GmbH, both temporal and local, depending on local geological and hydrogeological conditions, the state of remedial progress, remedial technologies in use and site specific procedures to treat contaminated waters. Mining influenced waters include:

- Mine waters;
- Seepage from mine dumps and tailings management areas;
- Waters processed in water treatment plants and subsequently discharged in a controlled manner to surface water bodies;
- Surface waters;
- Groundwaters.

Even the geogenic background concentration of Ra in waters varies from site to site as a consequence of local hydrogeological and geochemical conditions. Groundwaters not influenced by mining, for example, show ^{226}Ra background levels ranging around 10 mBq/L or less. Locally, up to 28 mBq/L ^{226}Ra were observed in a groundwater upstream flow (Aquifer 4) south of the Königstein deposit. Non-influenced surface waters typically show concentrations in the range of <5 to 20 mBq/L.

As part of the controlled flooding of the five Wismut GmbH mines, contaminated groundwaters are collected and piped to water treatment plants (in the order of 20 m^3/h and 1,000 m^3/h at the Pöhla and Schlema sites, respectively). Contaminated seepage from tailings management areas and mine dumps is processed in the same way. Table 7.8 illustrates typical ranges of ^{226}Ra concentrations in anthropogenically influenced waters (guidance values to illustrate orders of magnitude).

7.4.2.3. Exposure caused by ^{226}Ra at former mining and milling sites

During the remediation at U mining sites, ^{226}Ra contributes both directly and indirectly to the exposure of the population and of remediation workers. Direct exposure pathways include:

- Inhalation of ^{226}Ra contaminated dusts (in particular during intense physical remediation works);

TABLE 7.8. RADIUM IN MINING INFLUENCED WATERS AND IN WATER TREATMENT PLANT EFFLUENTS (MBQ/L)

Type of water	Origin/site	^{226}Ra concentration range	Comment
Flood water	From underground mines	2000–10 000	Site specific
Seepage	From mine dumps	20–1000	Site specific, depending on remediation progress, esp. type of cover
	From tailings sites	20–200	
Groundwater	Mine dump environment	100–low 1000s	
	Tailings sites environment	20–300	
Pore water	Tailings	500–3 000	
Treated water	Water treatment plant effluents	10–40	Technology specific and site specific
Surface water bodies	Downstream of mine water and water treatment plant effluent discharge	<10–30	Load specific, flowrate specific

- — Direct ingestion of contaminated solids (with a focus on children playing on mine dumps containing contaminated materials);
- — Consumption of drinking water and of contaminated foodstuffs (transfer of ^{226}Ra from soil and water into the food chain).

An indirect contribution of ^{226}Ra to exposure occurs via its daughter nuclides (^{222}Rn and its decay products in particular) through the following pathways:

- External radiation exposure;
- Inhalation of ^{222}Rn and its short lived daughter nuclides.

Figure 7.15 demonstrates the exposure situation at U mining and processing legacy sites. Exposure pathway analyses performed for the Wismut Rehabilitation Project document that inhalation of dust and direct ingestion typically contribute little to the radiological exposure of the public. In addition, worker doses are not dominated by these exposure pathways. In cases where contaminated foodstuffs are consumed, the ^{226}Ra contribution to dose via the aquatic pathway (drinking water consumption, irrigation, livestock watering) is both significant and greater than that of the U nuclides. This is a consequence of the relatively high transfer factors of ^{226}Ra in biota and of its significantly higher dose coefficients (g_{ing}) for ingestion (^{226}Ra: $g_{ing} = 2.8 \cdot 10^{-7}$ Sv/Bq; ^{238}U: $g_{ing} = 4.4 \cdot 10^{-8}$ Sv/Bq) [7.34].

The highest contribution of ^{226}Ra to radiation exposure is, however, through its decay nuclides. In this manner, external radiation from soils and residues is dominated by the decay products ^{214}Pb and ^{214}Bi. To determine a specific ^{226}Ra activity in soil for a given 2π geometry (quasi-infinite soil layer), one might proceed from the following relationship between the specific ^{226}Ra activity $a_{Ra\text{-}226}$ in soil and the ambient dose rate H*(10) at a level of 1 m above ground surface [7.35]:

$$H^*(10)\ (\text{in } \mu\text{Sv/h}) = 0.53\ a_{Ra\text{-}226}\ (\text{Bq/g}) + \text{BGr}\ (\mu\text{Sv/h}) \tag{7.2}$$

where BGr is the background value of ambient dose rate (contribution of cosmic radiation as well as of terrestrial radiation of natural radionuclides in soil [^{232}Th++, ^{238}U++,^{40}K], with both components together contributing to the BGr dose rate in the order of 100 nSv/h).

However, the most important dose contributor is via the emanation of the ^{226}Ra daughter nuclide and inert gas ^{222}Rn. At Schlema (Aue Operations) in Saxony, in particular, outdoor measurements performed before remediation was initiated revealed local mining induced radon concentrations which caused effective doses to the public in the order of up to 20 mSv annually.

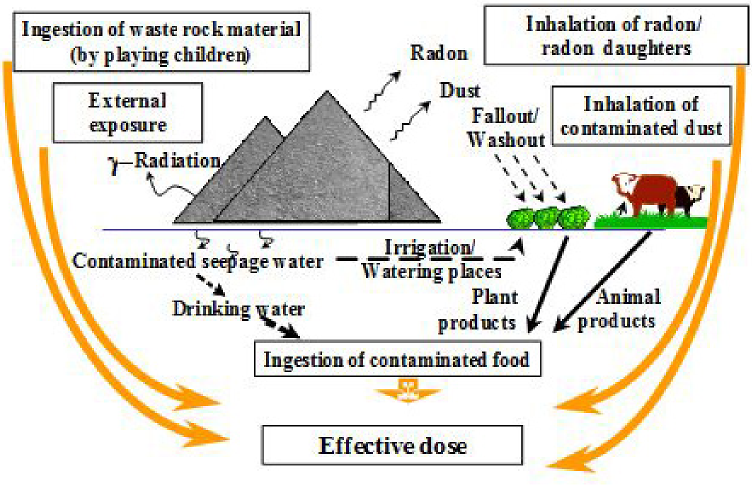


FIG. 7.15. Exposure pathways at a mine dump.

7.4.2.4. Remediation strategies with a special focus on radium

(a) Cover design to reduce gamma radiation

As part of the area remediation programme of Wismut, soil materials contaminated with ^{226}Ra were excavated and removed for containment within mine dumps or tailings management areas. In Germany, guidance levels underlying decision making on the removal of contaminated soils are specific: ^{226}Ra activities of <0.2 Bq/g are compatible with an unrestricted reuse of the area and 0.2–1.0 Bq/g with a restricted area use [7.36]. Mine dumps and tailings management areas, however, were remediated in situ and typically capped with a suitable cover of earthen materials. Both radiation transport calculations [7.37] and measurements performed on remediated mine dumps attest that a few decimetres of cover placed on top of soil contaminated with ^{226}Ra are sufficient to minimise the ambient dose rate to natural background levels (see Fig. 7.16 and Table 7.9 [7.37]).

(b) Cover design to mitigate the exhalation of ^{222}Rn

Approximately 43 million m³ of waste rock were piled up at the Schlema site in 20 mine dumps. A number of these dumps are located within a built up area or border on residential areas in the outskirts of the town. The piling up of

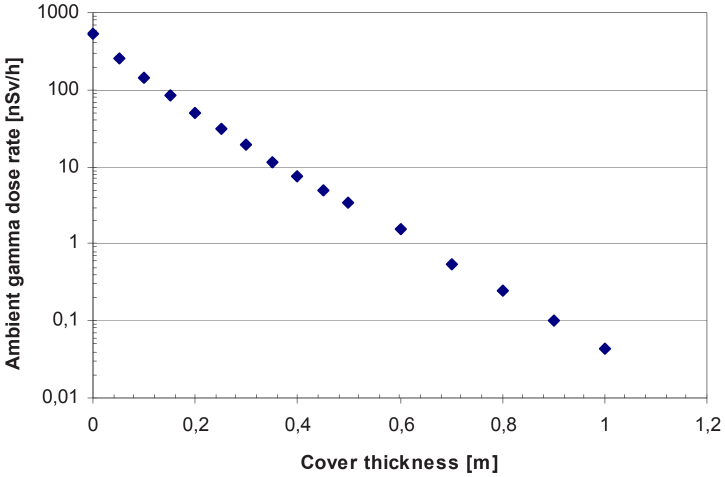


FIG. 7.16. Ambient gamma dose rate of ^{226}Ra induced gamma radiation from waste rock material of 1 Bq/g ^{226}Ra specific activity as a function of the thickness of a cover made of inert soil material.

mine dumps on long mountain slopes, the dump heights and the resulting steep slopes cause convective airflows within those dumps. The airflow is driven by temperature and air pressure gradients inside and outside the dumps. As a result of this, ^{222}Rn emerges at the foot of the dump during the summer months, whereas in winter high exhalation rates are observed on the dump plateau [7.38, 7.39].

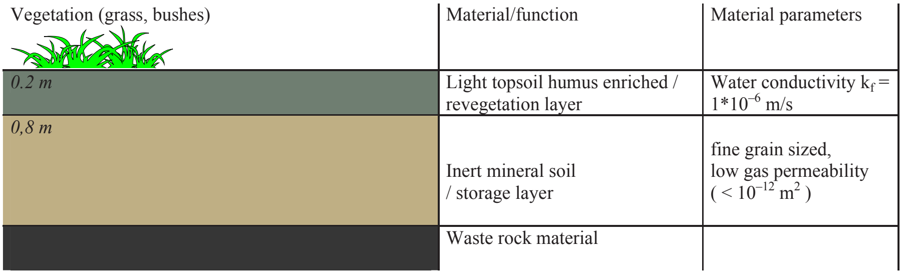
TABLE 7.9. RELATIVE ATTENUATION COEFFICIENTS AS A FUNCTION OF COVER THICKNESS

Cover thickness (m)	Attenuation (%)	Cover thickness (m)	Attenuation (%)
0.00	0.00	0.40	98.54
0.05	51.61	0.45	99.05
0.10	75.36	0.50	99.35
0.15	84.24	0.60	99.71
0.20	90.51	0.70	99.89
0.25	94.06	0.80	99.94
0.30	96.33	0.90	99.98
0.35	97.80	1.00	99.99

As a result of comprehensive investigations, Wismut has developed a mine dump cover design, the key element of which is a convection flow suppressing ^{222}Rn barrier. This barrier features gas permeabilities of $<10^{-12}$ m^2 (see Figs 7.16 and 7.17).

(c) Cover design to reduce infiltration rates and seepage of ^{226}Ra

The large tailings ponds at the former ore processing sites of Seelingstädt and Crossen and the radioactive tailings contained therein, as well as a number of mine dumps at the Ronneburg and Königstein sites, are capped with a multiple layer cover system. The purpose of this type of cover design is to reduce the rate of rainwater infiltration and hence the rate of seepage which in turn controls the release of contaminants (and hence also that of ^{226}Ra) from the tailings into ground and surface waters.



Vegetation (grass, bushes)	Material/function	Material parameters
0.2 m	Light topsoil humus enriched / revegetation layer	Water conductivity $k_f = 1*10^{-6}$ m/s
0,8 m	Inert mineral soil / storage layer	fine grain sized, low gas permeability (< 10^{-12} m^2)
	Waste rock material	

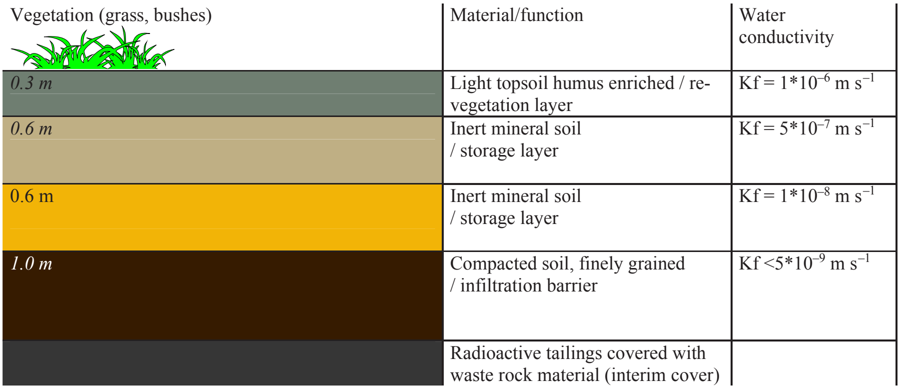
FIG. 7.17. Standard design of mine dump covers at the Schlema site.

FIG. 7.18. Mine dump #66/207 at the Schlema site before and after cover placement.

The key element of these multiple layer covers is a low water permeability (< 10^{-9} m/s) infiltration barrier. An overlying moisture storage layer supports the development of suitable vegetation with high evaporation rates. Figure 7.19 depicts a cross-section of the cover at the Trünzig tailings management area, while Fig. 7.20 shows the situation of the Trünzig tailings management area before remediation was initiated, and the present state of remedial progress at the site.

While it does have an effect on a number of contaminants (e.g. U, Th, As, Mn), the depicted cover option has no positive impact on the geochemical mobility of ^{226}Ra. In order to immobilize ^{226}Ra, additional substances will have to be included in the cover to initiate chemical reactions which in turn will bring about the precipitation and immobilization of ^{226}Ra.

This type of technology is applied to the construction of the cover of the Schüsselgrund dump of the former Königstein U mine. Contained in this mine dump are, among other substances, acidified sandstone from sulphuric acid leach U mining operations showing specific ^{226}Ra activities of a few Bq/g. As a consequence, pore waters within the dump are sulphuric. $Ca(OH)_2$ as well as $Ba(OH)_2$ are admixed to the mineral cover material whereby the cover acts as



Vegetation (grass, bushes)	Material/function	Water conductivity
0.3 m	Light topsoil humus enriched / re-vegetation layer	Kf = $1*10^{-6}$ m s^{-1}
0.6 m	Inert mineral soil / storage layer	Kf = $5*10^{-7}$ m s^{-1}
0.6 m	Inert mineral soil / storage layer	Kf = $1*10^{-8}$ m s^{-1}
1.0 m	Compacted soil, finely grained / infiltration barrier	Kf $<5*10^{-9}$ m s^{-1}
	Radioactive tailings covered with waste rock material (interim cover)	

FIG. 7.19. Cross-section of the cover of Trünzig TMA (Seelingstädt Operations).

FIG. 7.20. Trünzig TMA before remediation was initiated and the present state of remedial progress at the site.

a reactive element. The infiltrating rainwater picks up alkalinity as well as Ba ions and introduces them as reactive components into the dump body. While on the one hand, the buffering of sulphuric waters and the associated precipitation of iron, aluminium and heavy metals occur within the dump body, on the other hand barite is precipitated (in the presence of large quantities of sulphate) with co-precipitation and immobilization of Ra as Ra sulphate.

(d) Active water treatment

As documented in Table 7.9, both mine waters and seepage are contaminated with ^{226}Ra to such an extent that purification (water treatment) is required (by way of comparison, pursuant to radiation legislation applicable to the Wismut Project, only water showing ^{226}Ra levels of <0.7 Bq/L qualifies for discharge into surface water bodies).

Active water treatment technologies (i.e. featuring a continuous addition of chemicals) applied at the various sites differ with regard to the quality of waters, their contaminant inventory and local standards for the discharge of treated waters into receiving streams. The procedure to extract ^{226}Ra customary at almost all sites uses precipitation by the admixture of $BaCl_2$ to the feedwater to be treated. Insoluble $BaSO_4$ is precipitated in the water; ^{226}Ra is bound to this in the form of mixed crystals due to its physicochemical analogies to Ba. This stage of the process is typically combined with further precipitation stages, e.g. for As removal. The addition of a flocculation agent binds the produced primary flocs to well sedimentable macroflocs. Figure 7.20 depicts the water treatment flowsheet at the Schlema-Alberoda site, which integrates a precipitation stage for ^{226}Ra removal. Table 7.10 summarizes the ^{226}Ra related parameters of the Wismut water treatment units (annual averages).

TABLE 7.10. 226-Ra RELATED PARAMETERS OF ACTIVE WATER TREATMENT PLANTS

Site	Treatment capacity (m^3/h)	^{226}Ra concentration in water (Bq/L)		
		Untreated feedwater	Approved discharge	Actual discharge
Königstein	650	8.5/(6–10)[a]	(0.8)/0.4[b]	0.035
Schlema	1150	1.7	0.4	0.016
Helmsdorf	220	0.4/(0.1–1.4)	0.2	<0.01
Seelingstädt	380	0.06/(0.01–0.44)	(0.4)/0.2	<0.01
Ronneburg	500	0.1	0.2	0.01

[a] mean / (range)

[b] (maximum temporarily admissible) / mean admissible discharge value

Provisions have to be made for the storage of water treatment residues to ensure that the elevated contaminant levels contained therein (e.g. 20 Bq/g ^{226}Ra in the residues of the Schlema water treatment plant, but also 1000 Bq/g ^{238}U) will not be released during long term storage. This requires site specific solutions. At the Schlema site, for instance, water treatment residues are admixed with cement and other additives to form self-hardening geostable solidified waste. In this way, long term immobilization is provided for nearly all contaminants (including U, As, Mn and Fe). However, as the utilization of cement enhances ^{226}Ra

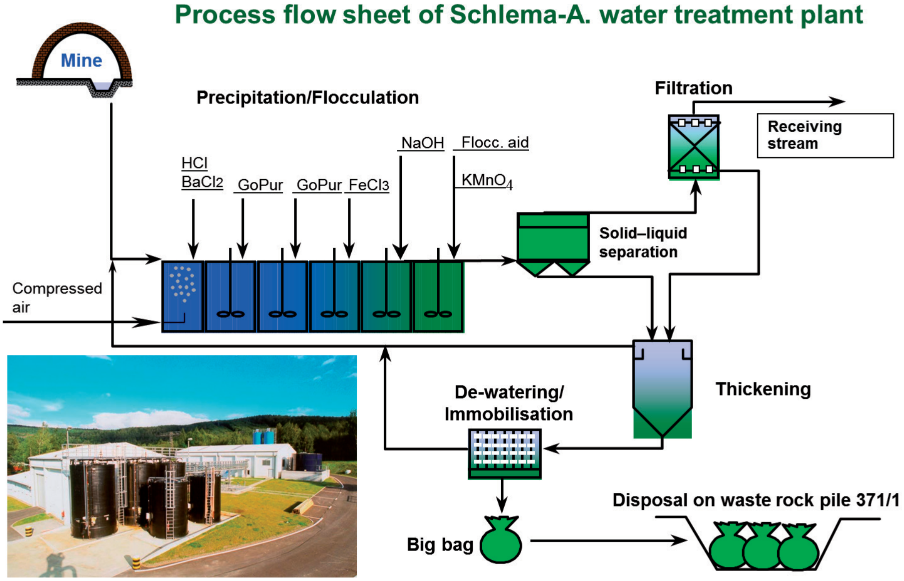


FIG. 7.21. ^{226}Ra removal in the course of complex water treatment at the Schlema WTP By BaCl$_2$ precipitation and flocculation using GoPur.

elution capacity, by way of sulphate reducing chemical reactions, the Schlema containment site is provided with additional technical barriers (base sealing, drainage system) to minimize the long term release of ^{226}Ra. At the Königstein site, the reactive cover materials capping the Schüsselgrund dump add Ca(OH)$_2$ as well as Ba(OH)$_2$ to the ^{226}Ra containing water treatment sludges. The resulting precipitation of Ba$_2$SO$_4$ causes immobilization of ^{226}Ra at the containment site (see also item (c) regarding seepage reduction).

(e) Passive water treatment

Pilot scale test runs of a passive biological unit for the treatment of mine flood water were initiated in 2004 at the Pöhla site (see Fig. 7.22). Referred to as constructed wetland, this unit has a treatment capacity of 20 m^3/h. The process stages were designed to remove Ra by macrophytic algae plus a reactive material, as well as for other purposes.

In the light of analyses performed so far, the activity concentration of ^{226}Ra within the algae material varies between approx. 10 Bq/g and 20 Bq/g dry matter. As is the case with all biological processes, the removal performance of the algae is controlled by boundary conditions such as weather conditions, incident light radiation, iron hydroxide deposition, canopy density and superficial extent.

FIG. 7.22. Pilot scale unit for the passive treatment of flood waters from the Pöhla mine.

Test results obtained so far do not fully document a satisfactory removal performance for ^{226}Ra. For this reason, a reactive process stage (known as a backup filter) was introduced downstream of the algae basin. The reactive material is in essence a granulated matter based on Ba sulphate. In practical operation, the set-up of an algae basin and backup filter meets regulatory standards for the discharge of treated water into receiving streams (see Table 7.10). The granulated matter achieves loading capacities of approximately 30 MBq/t.

(f) Monitoring and development of releases

Radium-226 is subject to permanent monitoring at all sites of the Wismut Project. Apart from ^{238}U or natural U, respectively, it is the most frequently measured radiological parameter. Within its basic monitoring programme, Wismut is currently operating 318 water measuring points, 28 dust measuring points and 33 dust precipitation measuring points where ^{226}Ra levels in environmental media are monitored on a monthly basis. This network is supplemented by 223 measuring points for ^{222}Rn. In addition to the basic monitoring programme, Wismut runs a temporary remediation monitoring programme under which ^{226}Ra measurements at selected remedial objects may go far beyond the scope of the basic monitoring programme.

Remediation progress is also reflected in the environmental monitoring results. By way of example, Fig. 7.23 documents the decrease of controlled ^{226}Ra releases into surface water bodies. This decrease is partly attributable to high performance water treatment plants coming on-line. In addition, the capping of mine dumps and tailings management areas also reduced ^{226}Ra loads released from these objects (either directly into receiving streams or via water treatment units). In parallel, a decrease of Ra levels in sediments and flood plains has become apparent.

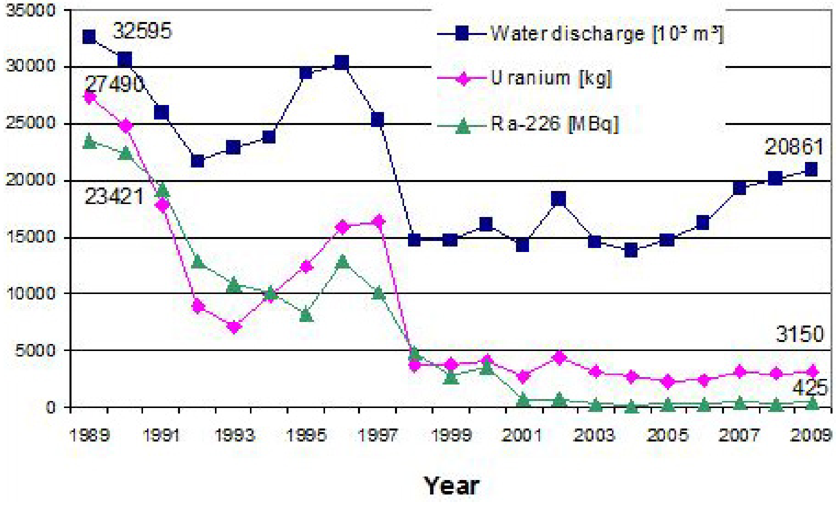


FIG. 7.23. Development of controlled discharge of ^{226}Ra into receiving streams (total of all Wismut sites, together with water discharges and controlled discharges of U).

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This publication is primarily intended to provide IAEA Member States with information for use in the radiological assessment of accidental releases and routine discharges of radium (Ra) in the environment. This report covers Ra behaviour in the terrestrial, freshwater and marine environments. The information presented here is relevant to the transfer of radionuclides through food chains to both humans and non-human biota. The corresponding remedial options and regulatory aspects also fall within the scope of this report. Additionally, applications of Ra isotopes as tracers in studies on environmental issues are discussed. This report can serve as a basis for remediation planning and identification of optimal remediation strategies in areas contaminated by Ra.

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