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Speciation of Radionuclides in the Environment

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Abstract

Methods for the determination of the speciation of radionuclides in aerosols, in aquatic solutions, in sediments, soils and rocks are reviewed. At present, most of the results about speciation are deduced from model calculations, model experiments, and separation of species (forms) of radionuclides, e.g., by sequential extraction procedures. Methods of direct determination of speciation of radionuclides (e.g., by laser induced spectroscopy) are in general not yet sensitive enough for a measurement of the very low concentrations of radionuclides in the environment. The methodological part of this paper is followed by a review of the very abundant literature about speciation of important radionuclides in the environment, i.e., in the atmosphere, hydrosphere and lithosphere. The review does not include the biosphere. Literature up to spring 1993 is included (with a few more recent additions).

1. Introduction

It is well established that the behaviour of radionuclides in the environment, their uptake by the biosphere and their toxicity are mainly determined by physical and chemical properties, i.e., their “speciation”, and to a lesser extent by their gross concentrations. The term “speciation” is used by different authors with a different meaning; it includes isotopic composition, physical form (e.g., a true solution, a solid, a species sorbed to a solid, a gas) and molecular composition. In this paper we define “speciation” in a rather broad sense as the physico-chemical forms of a radionuclide. The primary speciation of a radionuclide (and also of a non-radioactive element) is strongly dependent on its source. The later fate of the nuclides is influenced by the physical and chemical properties of the environment. For instance, the mobility of a nuclide in an aquifer depends strongly on the respective neutral, negative or positive charges and the composition of mineral surfaces and dissolved species. The primary species may change due to complexation or variations in pH and/or redox potential.

Despite the importance of speciation for the behaviour of nuclides in the environment and a very large number of investigations, our knowledge is still limited and much more work is needed. This peculiar situation results from the difficulties in the assessment of radionuclides at very low environmental concentrations and from problems related to the chemical

(e.g., sorption, ion exchange) and physical (i.e., radioactive decay) instability of many species. Immediately after their formation by nuclear reactions and/or radioactive decay, radionuclides exist as single, highly kinetically and electronically excited atoms or ions. The chemical behaviour at this state is very difficult to predict and to investigate. Very often it is even impossible to collect and analyse samples without changing the identity of the species. Many of the methods used to determine speciation are purely operational and may not identify the real species. An advantage of the determination of radionuclides as compared to non-radioactive trace elements is the practical absence of contamination during sampling and analysis. Nevertheless, very often the more extensive knowledge about the speciation of non-radioactive trace elements, e.g., [1] can be applied to radionuclides. Usually, under environmental conditions, there is time enough for radionuclides to acquire the speciation of stable isotopes; then they behave identically to the non-radioactive element. However, for some radionuclides (e.g., the actinides) no non-radioactive species exist.

The purpose of this paper is to review the present knowledge on speciation of relevant radionuclides in the environment, especially in the atmosphere, hydrosphere and lithosphere. Radionuclide speciation is influenced by the prevailing physical and chemical conditions in these compartments. The three compartments are interconnected. Radionuclides are transported by action of water and wind. The uptake of radionuclides by the biosphere depends largely on speciation in these compartments.

We discuss radionuclides of the natural decay series (e.g., decay products of ²³⁸U), important fission products and actinide elements. However, the restricted length of this paper allows only a relatively narrow and personally biased selection. The paper begins with a description of methods and processes which are presently used for the determination of speciation. With the recent availability of laser-based and other physical methods, new possibilities for sensitive in situ determinations have evolved. It is expected that these new methods will greatly enhance knowledge of speciation and will open further fields of applications. However, at the present state of the art the sensitivities of these new methods are often not high enough to assess the very low environmental concentrations of radionuclides.

Table 1. The main forms of radionuclides in environmental media and their possible characterization (in brackets)

| Medium | Forms |
|----------------------------|---|
| Atmosphere | Ions (nature) Gaseous molecules (nature) Aerosols (nature, radionuclide bonding) |
| Water | Ions (simple, complex, nature) Ion pairs (nature) Molecules (organic, inorganic, nature) Colloids (nature, radionuclide bonding) Particulate forms (nature of substrate, radionuclide bonding) |
| Sediments, soils and rocks | Dissolved forms in interstitial water or soil solution (characterization as above) Adsorbed forms (ions, molecules, nature of substrate and bonding) Coprecipitated forms (with oxidic coating, carbonates etc.) Bound with organic matter In crystal lattices of primary minerals (in lattice sites, interstitial) |

The methodological part is then followed by a discussion of radionuclide speciation in the *atmosphere*, *hydrosphere* and *lithosphere*. We do, however, not discuss radionuclide speciation in the biosphere.

2. Methods for the determination of speciation

Methods of analysis of speciation of radionuclides in the environment are generally similar to those used for non-radioactive (stable) trace elements, except for some differences due to the unstable nature of radionuclides, their extremely low concentrations in most environmental samples and the radiation emitted. Therefore, much information can be obtained from books on the environmental speciation of stable trace elements, e.g., [1–4]. Only few review articles or books focus on the speciation methods for radionuclides [5–7].

The *methods* can be classified into three categories: *thermodynamic (and kinetic) calculations*, *direct analysis* of environmental samples (including in situ analysis) and *model experiments* (experimental simulation in the laboratory). The individual methods and their applications strongly depend on the nature of the medium to be analyzed, and on the different physico-chemical forms (species) to be determined. Table 1 summarizes the main forms of radionuclides often distinguished in different environmental media and indicates possibilities for further characterization. The discussion of the methods will follow the outline of this table.

2.1 Model calculations

These methods use thermodynamic (equilibrium) and kinetic data for the calculation of the distribution of phases and species from a known composition and

other parameters (pH, redox potential, temperature, etc.) of the system. The methods have been extensively developed, particularly for aquatic systems [8, 9] and can range from rather simple procedures involving one element and several ligands or phases, to very complex computer programs. The simple procedures are often inadequate to account for the complex nature of processes involved in determining the speciation of radionuclides and therefore yield rather inaccurate results.

However, even with computer calculations, serious difficulties can arise for the following reasons: 1) many of the necessary thermodynamic data are missing or are unreliable, as reflected in the large spread of available data. For instance, for actinides the thermodynamic data are still poorly known and it is often questionable whether relevant natural species have been included for the calculations. Thermodynamic data are usually determined in well defined laboratory systems (i.e., in NaClO₄ solutions); 2) the concentrations of radionuclides are often too small to reach saturation limits and there are plenty of sorption sites available (e.g., on glass walls) for species at these low concentrations; 3) fulvic and humic substances which are often present in natural systems are ill defined, and their complex formation constants are poorly known; 4) sometimes humic substances form colloids. Natural colloids are very difficult to include in model calculations, but may be of considerable importance for radionuclide speciation; 5) it is also very difficult to estimate sorption site densities in heterogeneous systems. Therefore, despite the usefulness of these model calculations it is strongly recommended to perform, *in addition*, measurements in the laboratory *and* in the real world. For further details we refer to a recent book by Kramer and Allen [3] or directly to the manuals of the computer codes.

There is a general lack of information on the *kinetics* of environmental processes, and therefore most of the calculations assume equilibrium systems; many processes are biologically mediated, e.g., [10], and chemical equilibration and kinetics may change. The compositions, abundances, and properties of many components of natural systems are poorly known. This applies particularly to natural organic matter and colloidal components. Consequently, the results obtained by calculations can be considered only as approximation of the actual speciation of the studied radionuclides or as denoting the state towards which the system tends to equilibrate. There is no doubt, however, that the information gained from such calculations should be examined at the beginning of any speciation study because it can greatly facilitate the ensuing experimental analysis.

A large number of data were calculated for speciation of radionuclides in aquatic systems, e.g., [11–16]. Many calculations also included adsorption on solid phases present in the system. Less information was obtained by this method on radionuclides in soils, e.g., [17], and in the atmosphere [18, 19, 20, 21]. The latter

application involved mainly efforts to predict the release of radionuclides from nuclear accidents. In the interpretation of data obtained in this way, it should be kept in mind that thermodynamic calculations cannot account for effects of atomic recoil and hot atom chemistry, and only to a limited extent for effects of radiolysis which can inflict changes, namely in the speciation of radionuclides in environmental solids; less often the aqueous speciation is also affected [22, 23].

Computer codes, e.g., MINEQL [24], MINTEQA2 [25], PHREEQE [26], EQ3NR [27], etc., are available for these calculations. PHREEQE is based on ion-pairing and can calculate pH, redox potential, and mass transfer. It can calculate speciation and the composition of solutions in equilibrium with multiple phases. The program includes elements, aqueous species, and mineral phases. MINTEQA2 is a U.S.E.P.A. geochemical speciation model capable of computing equilibria among dissolved, adsorbed, solid, and gas phases in an environmental setting. It contains an extensive and reliable thermodynamic data base. These computer codes may be combined with surface complexation models [28, 29, 30] to obtain interactions between surfaces and dissolved species. The MINTEQA2 program includes several possibilities of surface complexation. The quality of such calculations depends strongly on selection of realistic chemical processes.

Very important information about speciation can be obtained from Eh-pH diagrams. Brookins [31] has published an extensive compilation of such diagrams of importance to geochemistry. His work includes also diagrams for actinide elements.

2.2 A direct experimental analysis of environmental samples

is the most straightforward, and often the best approach to the investigation of speciation. However, it is often connected with a number of difficult problems [4, 32, 33]. The first problem is sampling, sample storage and pre-treatment. These procedures should not change the speciation of radionuclides, a condition which is often difficult to fulfil. The analytical procedure itself can affect speciation by shifts in equilibrium or, more specifically, by changes in the ratio of various forms of radionuclides in the sample. Consequently, only such speciation procedures should be used that affect these ratios as little as possible. A serious problem can arise from adsorption of radionuclides to walls of equipment and other surfaces of the analyzed system. A simultaneous presence of three or more radionuclide species in comparable quantities generally makes an analysis very difficult, particularly if the selectivity of separation or the distinction between the species is poor.

Owing to these difficulties, it is, with the currently available experimental techniques, only possible to classify the speciation of radionuclides into operationally defined classes based on their thermodynamic

Table 2. Direct methods for speciation analysis [after 36]

| Method | Applicability | Concentration range |
|--|------------------------|---------------------------------|
| <i>Non-invasive methods</i> (no pre-treatments, no separations) | | |
| IR spectroscopy | solids, liquids, gases | $>10^{-6}$ -10^{-4} mol/L |
| UV-VIS spectroscopy | solid, liquids, gases | $>10^{-7}$ -10^{-5} mol/L |
| Fluorescence spectroscopy | solids, liquids | $>10^{-8}$ mol/L |
| Raman spectroscopy | solids, liquids, gases | $>10^{-5}$ mol/L |
| Photoelectron spectroscopy | solids | $>10^{-5}$ g/g |
| Photoacoustic spectroscopy (LIPAS) | solids, liquids | $>10^{-12}$ mol/L |
| Thermal lensing spectroscopy (LITLS) | solids, liquids | $>10^{-10}$ mol/L |
| Rutherford backscattering | solids, thin layers | $>10^{-5}$ g/g |
| Powder diffraction | solids, aerosols | $>10^{-4}$ g/g |
| NMR spectroscopy | solids | $>10^{-6}$ g/g |
| Mössbauer spectroscopy | solids | $>10^{-6}$ g/g |
| <i>Invasive methods</i> (pre-treatment, separations) | | |
| Electrochemical methods (polarography, potentiometry, voltammetry) | solutions | $>10^{-10}$ -10^{-9} mol/L |
| Chromatographic methods | solution, gases | |
| Ion exchange methods | solutions | |
| Electrophoresis | solutions | |
| Extractions | solutions | |
| Precipitation, co-precipitations | solutions | |

or kinetic behaviour in the sample. Usually, no single technique can give unequivocal information on speciation, and, therefore, it is advantageous to combine two or more techniques. Sometimes the techniques are combined in speciation schemes [34]. No general speciation schemes can be recommended, as they depend on the nature and character of the environmental samples. However, most of the schemes include, as a first step, the separation of phases (solid-liquid, gas-solid, gas-liquid) which is often carried out routinely during sampling. Possible methods for direct speciation analysis are given in Table 2.

2.2.1 Methods for direct speciation analysis of aerosols

A compilation of methods for the characterization of (radioactive) aerosols was published by Nichols and Bowsher [35]. Up to now, only limited efforts have been made in the nuclear field to determine atmospheric speciation (most of the given references are for inactive aerosols), but the techniques and methods for inactive aerosol analysis can be adapted for (highly) radioactive samples. Both, standard wet chemistry, and specialized analytical techniques, were used to identify speciation in aerosols. Here, we discuss some instrumental techniques without aiming for completeness.

Infrared spectroscopy determines chemical species from characteristic vibrational spectra of IR absorp-

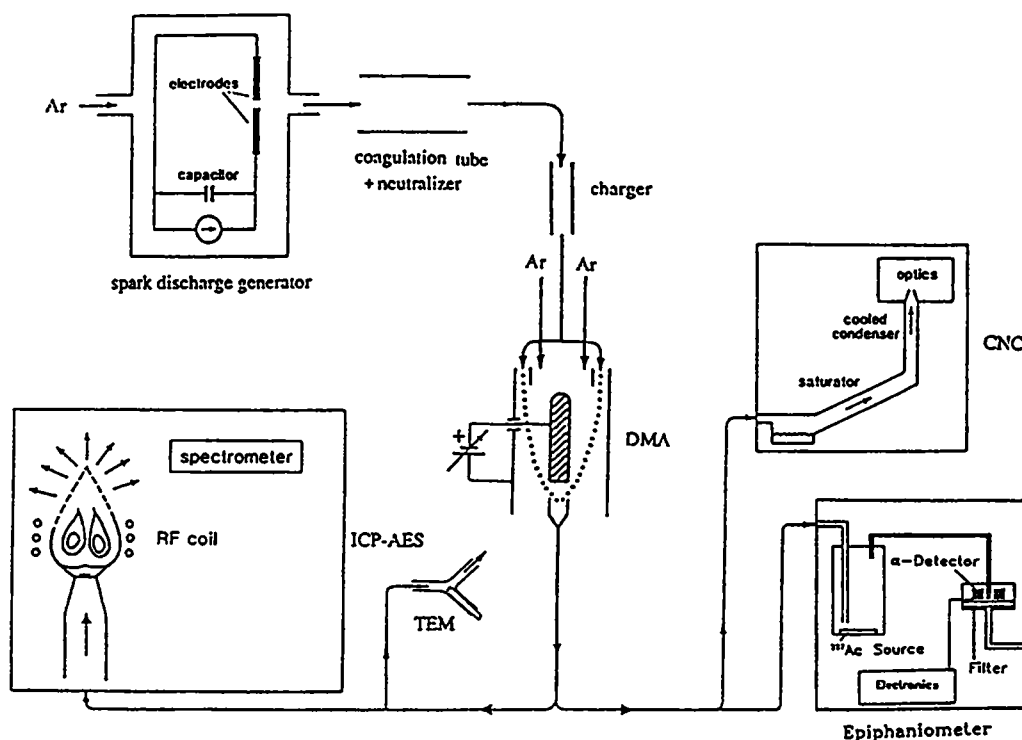


Fig. 1. In situ determination of structure and composition of particles and agglomerates [45]. Top left: aerosol generator; middle: DMA (differential mobility analyser); bottom left ICP-AES spectrometer; top right CNC (condensed nuclei counter); bottom right: epiphaniometer.

tion. Fourier transform techniques have significantly improved the sensitivity to <1 ng. It is suitable for surface analysis of aerosols. Raman spectroscopy gives information on the molecular structure of polarizable compounds. *Interference Enhanced Raman Scattering* permits the study of very thin films (<5 nm) and opens the possibility to characterize radionuclides adsorbed to surfaces of aerosol particles [37].

The chemical composition of aerosols can be determined by *X-Ray Diffraction (XRD)*. In combination with *Scanning Electron Microscopy (SEM/EDAX)* it offers the possibility to determine the physico-chemical form of an aerosol. *X-ray Photoelectron Spectroscopy (XPS)* investigates the binding energies of ejected electrons. The technique is suited to study oxidation processes of aerosols. It can also be used to monitor the adsorption and desorption of water molecules from aerosols.

Various mass spectrometric techniques are used to investigate chemical speciation of aerosols. *SIMS (Secondary-Ion Mass Spectrometry)* can be combined with *Auger Electron Spectroscopy (AES)* and *XPS*, SIMS is sensitive to matrix interferences and its sensitivity for different elements can vary by orders of magnitude. Individual aerosol particles were analysed by *LAMMA (Laser Microprobe Mass Analysis)* [38]. In a reduced power mode, the laser can be used to desorb molecular ions from surfaces of particles to provide chemical information on adsorbed species. A quantita-

tive analysis is, however, extremely difficult. In the *PAMS (Particle Analysis Mass Spectrometry)* technique [39], airborne particles are directly injected into the ion source of a mass spectrometer and can be analysed with very high sensitivity.

Electron Energy Loss Spectroscopy (EELS), [40] gives information on chemical composition, oxidation states, bond distances, and electron structures of aerosol particles. Incident electrons suffer energy losses which depend on electronic and chemical composition of the sample. Electron diffraction combined with *TEM (Transmission Electron Microscopy)* provides very useful information on the microscopic (beam diameter 0.04 mm) chemical composition of particles [41]. The method is very powerful, but time consuming.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) was used to analyze the chemical composition of aerosol particles [42]. Aerosols were directly introduced into an ICP. At low concentration the emission signal was observed as a flash for each particle. The particle concentration and chemical composition can be measured simultaneously.

A very interesting further application of ICPAES, in combination with other methods, has been performed by [43]. These authors combined a *Differential Mobility Analyser (DMA)*, with an ICPAES spectrometer, a *Condensed Nuclei Counter (CNC)*, counts particle number) and a *Surface Analyser (Epiphani-*

ometer), [44, 45], Fig. 1. The epiphaniometer [46] uses neutral ^{211}Pb atoms recoiling from a ^{227}Ac source to label aerosol particles which are detected by α -decay (^{211}Bi in radioactive equilibrium with ^{211}Pb). This instrumental arrangement enabled simultaneous measurements of mass, surface and mobility diameter of Ag-agglomerates.

2.2.2 Methods for direct speciation analysis in the hydrosphere

Sampling, sample storage and speciation techniques for trace elements have been well treated in numerous review articles, e.g., [4, 32, 33, 47–49]. Here, only the peculiarities of the speciation analysis for radionuclides, as well as recently developed techniques will be discussed. Despite the usually very low concentrations of radionuclides in environmental samples, there is a considerably smaller possibility to contaminate the samples (by radionuclides) during sampling and analysis than in the analysis of trace elements. On the other hand, the low concentrations preclude the use of some analytical techniques, whereas other techniques require pre-concentrations in order to increase the sensitivities for detection by radioactivity measurement. It is recommended to use pre-concentration techniques which do not interfere with equilibrium.

Typical examples are continuous flow centrifugation [50, 51], or large volume filtration [51, 52] which separate and concentrate particulate forms. Both techniques belong to the group of 'physical separation' methods. This group also includes ultra-filtration, dialysis, diafiltration, electro dialysis, sedimentation, discontinuous (ultra)centrifugation, diffusion, adsorption chromatography, gel filtration, and size exclusion chromatography, foam flotation, volatilization and electrophoresis [34, 53, 54]. The separation of physico-chemical forms of radionuclides is based on differences in size, charge, density or other properties. Selective separation can only be achieved when equilibration among species proceeds much slower than their separation.

The first two physical separation methods from above, and, in addition, ultra-filtration with hollow fiber filters [55], or cassette systems [56], dialysis with concentration on ion exchangers [48, 57], sedimentation (also in situ, [58]), and foam flotation [47, 59, 60] are suitable for applications to large volumes and, therefore, for the analysis of low concentrations of radionuclides. However, these methods may be hampered by membrane clogging [49, 61, 62], by possible concentration polarization effects [34], and by adsorption [32, 62]. The other methods from above are seldom applicable for a direct analysis of speciation of radionuclides at environmental concentrations, as they enable only a treatment of small volumes of water (as e.g., interstitial waters or pore waters in sediments or unsaturated soils). Examples of the application of

paper electrophoresis (after pre-concentration of contaminated groundwaters by evaporation), size exclusion chromatography, or small-volume ultra-filtration can be found [63, 64]. Ultra-filtration and ultra-centrifugation can be used to distinguish between dissolved and colloidal species. Since colloids represent a delicate metastable state of matter, even these simple operations may affect the system due to changes in ionic strength, pH, and Eh. Procedures for sampling and characterization of colloids and particles have been reviewed by McCarthy and Degueldre [65].

Further pre-concentration methods for speciation analysis are based on adsorption, co-precipitation, ion exchange, solvent extraction and electrodeposition. The separation of individual radionuclide species is possible, because of their different chemical behaviour. Except for co-precipitation, the concentration from large volumes of water can be best performed by a flow-through arrangement, e.g., with an extractant fixed on a support. Due to its slowness, the separation by electrodeposition was seldom used for pre-concentration [66]. The co-precipitation method proved particularly useful for separation of different oxidation states of radionuclides in natural waters [67–69]. For instance, co-precipitation with praseodymium fluoride, or zirconium iodate, was used for separations of Pu(III) and Pu(IV) from Pu in higher valence states [70]. The selectivity of separation of ionic, from colloidal species, by this method may be doubtful. Techniques capable of separation/pre-concentration of radionuclide species from large volumes of water are sometimes combined in 'large volume samplers' [12, 71, 72]. For instance, the Batelle large volume water sampler combines in-line filtration (0.4- μm Nuclepore®) with anion and/or cation exchange and adsorption on Al_2O_3 . The sampler enables processing of up to 4000 L of water in 3 hours [73]. A very efficient separation of radionuclides from large water samples can be achieved by MnO_2 impregnated filters. This technique is the preferred method for the pre-concentration from large volumes of water of very low concentrations of fallout radionuclides, particularly plutonium and americium (e.g., [74, 75]).

Other methods which enable working only with smaller volumes of water, can exceptionally be used for a direct speciation analysis of environmental radionuclides. Among these methods are high performance liquid chromatography (HPLC, with pre-concentration, [64]), batch arrangements for adsorption [67], ion exchange [64, 70], and solvent extraction [70]. These methods are very useful in *model experiments* (see below), and can be used for an analysis of contaminated or waste waters [64, 76].

Until recently, virtually no methods were available for a direct detection of chemical species of radionuclides in environmental water samples. Voltammetric and other electrochemical methods (ion selective electrodes) cannot be used for this purpose, and radiopolarography [77] is not sensitive enough. *Spectroscopic methods* are very suitable for the determi-

nation of speciation, however, *classical UV-VIS-NIR* spectroscopy is often not sensitive enough to measure the very low concentrations of radionuclides in environmental samples.

Laser- and X-ray-induced spectroscopic methods and new techniques for detection have improved this situation considerably, but can only be performed by highly specialized laboratories [78–81]. In the following we give a short description of some of these methods.

Laser-Induced Thermal Lensing Spectroscopy (LITLS), [82]. A laser beam, exactly tuned to excite a well defined energy level in the species of interest, creates a local temperature gradient in an absorbing medium. The temperature gradient induces changes in the refraction of the system. The spatial distribution of the refractive index acts like a thin optical lens and defocuses the laser beam. The method is capable for a determination of dissolved uranyl ions with a sensitivity of 4×10^{-6} mol/L. The adjustment of two exactly collinear laser beams is difficult. Improvements of the method are expected.

Laser-Induced Photoacoustic Spectrometry (LIPAS), [83]. Absorbed photons excite electronic levels which decay by radiative or non-radiative processes. This leads to heating of the light-absorbing species. The temperature change induces a pressure wave which is detected with a piezo-electric crystal. The photoacoustic signal is proportional to the concentration of the analysed species in solution. The sensitivity is about three orders of magnitude better than in conventional spectrophotometry. The method has also been used for non-radioactive trace elements [84]. For uranium in aqueous solutions, a sensitivity of 10^{-4} mol/L was reached [79].

X-ray Absorption Near-Edge Spectroscopy (XANES). X-rays, generated by synchrotron radiation [85] are absorbed in the sample of interest. Near the characteristic absorption edge (e.g., K, L, etc.), a step like increase in absorption occurs when an electron is excited to an unbound continuum. The position of the absorption edge is element-specific, but depends also on the chemical bonding. Fine structure near the absorption edge allows to gain insight to oxidation states and electronic levels.

The method of *Extended X-ray Absorption Fine Structure (EXAFS)* uses synchrotron radiation [86]. At energies about 50 eV above the main absorption edge, one observes oscillations in the absorption coefficient. This is due to interferences between ejected photoelectrons and surrounding atoms. It enables to estimate distances between an element and its neighbours, and with some limitations the corresponding coordination numbers.

Unfortunately, at present, the synchrotron radiation methods are not sensitive enough to investigate the very low environmental concentrations of actinides. However, a new generation of synchrotrons, now under construction, will improve this situation considerably.

2.2.3 Methods for direct speciation analysis in the lithosphere

Methods for the analysis of dissolved species of radionuclides in interstitial water and soil solutions are similar to those discussed above for the hydrosphere. Their application can, however, seriously be complicated by the small volumes of water available and by possible shifts in equilibrium during sampling, which is often more pronounced due to the separation of the sample from the porous solid phase. The sampling problems are discussed in some detail elsewhere [87, 88]. Larger volumes of soil solution are more easily obtained with lysimeters.

Methods for determination of radionuclide species associated with the solid phase of sediments, soils and rocks can be classified into three groups: *leaching procedures* (also called ‘chemical extraction’ or ‘selective dissolution’), *correlation analyses and special techniques*. They can be applied either on the whole samples (usually homogenized), or on fractions of the sample, separated by differences in size, density or other properties of the solid phases. When carrying out separations, it is necessary to consider possible effects on the speciation. This applies also to other kinds of solid sample treatments. Comprehensive discussions of sampling and processing of solid samples for speciation analysis were given by Batley [4], Jenne *et al.* [89], and Thomson *et al.* [90].

The most frequently used method for analysis of speciation in the solid phase is ‘*selective leaching*’ of the radionuclides of interest by a solvent or a solution. The principle and limitations of this method have been described by, e.g., Jenne and Luoma [91], Luoma and Bryan [92], Pickering [93], and Kersten and Foerstner [94]. The methods aim at extraction of different species of radionuclides based on selective desorption of adsorbed or ‘exchangeable’ forms, or on selective dissolution of a solid phase containing the radionuclide. Many different leaching procedures were used for the analysis of speciation of radionuclides. They range from simple extractions with a single extractant [95–97], through parallel extractions with several extractants [98–103], to complicated multistage sequential procedures [102, 104–111].

Table 3 presents several examples for sequential procedures. The procedures differ in significance and/or order of individual extraction steps, but most often the following forms are distinguished: *free-bound or exchangeable*, *bound in carbonates*, *associated with Fe and Mn (hydr)oxidic coatings*, *associated with organic matter* and *residual forms in crystal lattices of minerals*. Some authors [64, 103] included *isotope exchange* with stable isotopes as an extraction step for radionuclides to determine exchangeable forms.

The extractions are evaluated either from the concentrations of radionuclides in individual extracted fractions or from the difference between radionuclide concentrations in the analyzed solids before and after the extraction. The extracts are usually analyzed for

Table 3. Examples [104, 107, 108, 111, 117] of sequential extraction procedures used in the analysis of speciation of radionuclides in soils and sediments

| Step No. | Composition of leaching solution | | | | |
|----------|---|--|--|------------------------|--|
| | [117] | [104] | [107] | [108] | [111] |
| 1 | 1 M MgCl ₂ | 0.1 M NaCl | 0.05 M CaCl ₂ | H ₂ O | 1 M MgCl ₂ |
| 2 | 1 M NaAc pH 5 (+HAc) | 1 M HCl | 0.5 M HAc | 1 M NH ₄ Ac | 0.1 M NaOH |
| 3 | 0.04 M NH ₂ OH · HCl +25% HAc | 0.11 M EDTA +1.7 M NH ₄ OH | 0.1 M Na ₄ P ₂ O ₇ | 6 N HCl | 0.2 M (NH ₄) ₂ Ox +0.2 M H ₂ Ox |
| 4 | 0.02 M HNO ₃ +30% H ₂ O ₂ | acid digestion | 0.175 M (NH ₄) ₂ Ox +0.1 M H ₂ Ox | acid digestion | 1 M NaAc pH 5 (+HAc) |
| 5 | acid digestion | — | — | — | 0.175 M NaCit +5% Na ₂ S ₂ O ₃ |

Abbreviations: Ac - acetate, Cit - citrate, Ox - oxalate.

radionuclides without further separation of species. However, additional separations of the extracted species using gel chromatography [112], ultra-filtration [113], or co-precipitation [114] have been described. It is very important to avoid an extensive pre-treatment of the solid sample. For instance, grinding or drying of sediments may change the leachability of radionuclides [115]. On the other hand, a fractionation of the sample according to grain size or mineralogic composition, prior to the extraction, may ease the interpretation of the results [64].

The biggest problem with leaching procedures is low selectivity of the extractions for several reasons:

- The extractants often do not quantitatively release the expected form(s), but also attack unwanted forms of radionuclides.
- The extractions may significantly change the abundances or properties of unextracted components in the sample.
- The extracted radionuclides can re-adsorb on the residue.

The importance of the mentioned criteria depends on the duration of extraction, the solid/extractant ratio, the composition of the analyzed solid, and, with the exception of (b), on the chemical nature of the radionuclides present. This virtually eliminates the possibility of corrections to phenomena (a)–(c) and makes an accurate characterization of the extracted forms difficult. Probably, the most ill defined category is the 'exchangeable' fraction of a radionuclide.

Other problems are connected with surface coatings of solid grains ('armouring', [91]), mutual effects of components of the solids, etc. Due to these problems, it is obvious that the most reliable characterization of the speciation of a radionuclide in a sample can be obtained using 'tailored' leaching procedures, where the properties of radionuclides and sample are properly taken into account, and possible complications are experimentally checked. But tailored leaching procedures make a comparison of results obtained by different methods and different authors difficult. For comparisons, 'standard' extraction methods are

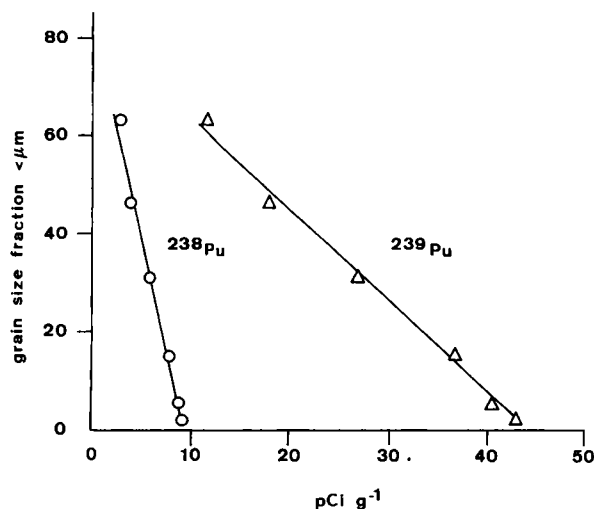


Fig. 2. Plot of ²³⁸Pu and ²³⁹Pu concentration (pCi/g) in grain size fractions (μm) of sediments from Wyre Estuary [122].

more useful, for instance, those proposed by Salomons and Foerstner [116] or by Tessier *et al.* [117]. The latter method represents at present the most frequently used sequential extraction procedure.

Methods of **correlation analysis** are based on the study of correlations between the concentration of a radionuclide in a series of samples and characteristic parameters of the samples. Conclusions on the character of bonding of a radionuclide can often be drawn from correlations, unless large variations in the concentration of the radionuclide occur for other reasons than variations in the properties of the solid phase.

The most frequently used correlation involves the size of soils or sediment grains. To avoid possible complications by different levels of contamination of samples from different locations, correlations are usually carried out with subsamples obtained by sieving or sedimentation. In most cases, the concentrations of radionuclides were observed to decrease with increasing particle sizes [118–125]. This is illustrated in Fig. 2. The decrease has often been considered as an indication of the siting of a radionuclide on the surface

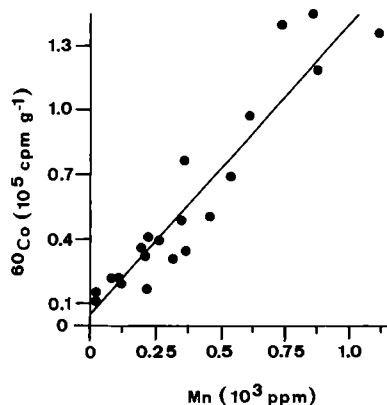


Fig. 3. Concentration of ^{60}Co vs. total manganese concentration in size-fractionated soils from a well near to a radioactive waste disposal trench at Oak Ridge National Laboratory [128].

of solid particles [123], etc., or as evidence of absence of strong associations of radionuclides with distinct phases in the sample (e.g., clays, [63]). Accordingly, variations in the association of different radionuclides with different particle sizes and density fractions of sediments can be interpreted as due to dissimilar binding mechanisms of the radionuclides [121, 126].

Further parameters considered in correlation analysis are chemical or mineralogical compositions of the samples. For instance, MacKenzie [127] found a significant correlation between contents of ^{137}Cs and aluminium in vertical profiles of lake or estuarine sediments in Scotland. He interpreted the correlation as indicative for the association of ^{137}Cs with clay minerals, whose abundance in the sediments was assumed to be proportional to the Al content. Very convincing conclusions from correlation analysis were drawn by Means *et al.* [119, 128] for radionuclide and manganese concentrations in size fractionated soils, contaminated by disposal of radioactive wastes at ORNL. Fig. 3 illustrates one of these correlation analyses.

High correlation coefficients indicated associations of ^{60}Co ($r = 0.9535$, $n = 20$) and actinides ($r = 0.8398$, $n = 20$) with manganese oxide coatings of soil grains. Correlations of these radionuclides with iron oxides, or organic carbon contents were poor or negative. A strong positive correlation was found by Aston *et al.* [122] between plutonium and organic carbon contents in estuarine sediments ($r = 0.85$). However, the authors warned that the correlation might be due to a similar dependence of both parameters on grain size/surface area characteristics of the sediments. This points to the limitations or pit-falls of the speciation analysis based on correlations.

Among *special techniques* for the analysis of speciation of radionuclides in solids are various kinds of autoradiography, and procedures based on the measurement of radionuclides in separated and identified components of the solid phase. These techniques aim at the study of the association of radionuclides with individual mineral grains, or of spatial distributions of radionuclides in the solid phase. The analysis can be

performed by simple means, like microscopic picking, or other separations of well characterized components [64, 94, 129], as well as by sophisticated experimental procedures, like fission track autoradiography in mica detectors [130], fission track mapping and delayed-neutron counting [131], or dispersed-grain nuclear emulsion techniques [132]. Demchuk *et al.* [133] used contact autoradiography, in combination with microscopy, for characterization of hot particles from the fall-out of Chernobyl.

2.3 Model experiments

Model experiments represent the analysis of natural radionuclide speciation and/or behaviour in artificially prepared systems simulating natural systems, or in environmental samples modified to simplify analysis. The main advantages compared to direct analysis of environmental samples, are the easier interpretation of results, and the possibility of examining speciation and behaviour under broader and/or better defined conditions. The experiments often aim at obtaining data for thermodynamic calculations, or at verifications of conclusions drawn from such calculations. Because model experiments are almost always carried out with identical, or isotopic radionuclides, they can be denoted as radio-tracer methods of speciation analysis. The radio-tracer method with isotopic labelling was frequently also used for studies of speciation and behaviour of stable trace elements, e.g., [32, 134–137]. Only exceptionally model experiments were made with a non-isotopic or stable analogue of a radionuclide (e.g., europium for actinides, [138]). The actual realization of model experiments depends on the environmental medium studied.

2.3.1 Model experiments for the speciation of aerosols

In this medium the experimental modelling usually consists in artificial preparation of radio-aerosols and their subsequent study. This approach has recently been used, namely for modelling forms of radionuclides released during a major nuclear accident [139, 140, 141].

2.3.2 Model experiments for aqueous speciation

In modelling speciation in water, the radionuclide (or an isotope) is usually added in well defined speciation to a sample of filtered or unfiltered water and its behaviour is analyzed. If the speciation of the radionuclide is the same as the added radiotracer, then both, tracer and nuclide should behave similarly. This method was successfully applied for investigations of biological material [142], but is expected to be more complex and not unequivocal for heterogeneous environmental samples. Alternatively, artificially prepared solutions are used to simulate natural waters. This ap-

proach enables using a large spectrum of speciation techniques, including those applicable for small volumes of water. Some of the techniques ensure that disturbances of chemical equilibrium are avoided, kept at minimum or do not affect speciation analysis.

Particularly suitable for this purpose are various spectroscopic methods (e.g., LIPAS, etc., see above), free-liquid electrophoresis [7, 143], diffusion [144], and special methods of solvent extraction [145]. Relatively rapid physical separation methods like centrifugation, filtration and ultra-filtration [36, 146] in small-volume arrangements do often not significantly disturb the equilibrium, either. When using other methods, possible influences on solution equilibrium should be checked. Under these conditions, high performance liquid chromatography (HPLC; [147]), solvent extraction [69, 148, 149], ion exchange [148, 150], gel chromatography [148, 151], paper chromatography [152], and adsorption [153, 154] were successfully used for analysis of speciation of radionuclides in natural and waste waters.

Caution must be taken in the planning and evaluating of model experiments. The addition of a radionuclide to natural water samples should not change the pH, and the concentrations of the added (dissolved) radionuclides should be close to its modelled concentration (i.e., ionic strength), otherwise the concentration dependency of speciation should be checked. Even then, the speciation of the added radionuclide does not necessarily simulate the speciation of naturally present radionuclides, because of slow equilibration [134], etc. It is, therefore, imperative to study the time-dependency of speciation in the labelled water.

Slow equilibration is particularly encountered if the added radionuclide is adsorbed by suspended particles, or if it forms colloids or kinetically stable complexes. Slow changes in speciation of added radionuclides can sometimes be used for a characterization of the species formed [155].

2.3.3 Model experiments for the speciation in sediments, soils and rocks

The use of model experiments for the analysis of speciation of radionuclides in environmental solids usually consists in a laboratory study of the distribution of radionuclides between a solid phase and a solution, or the distribution of a radionuclide-label in a labelled solid phase. A large number of papers has been published on model experiments, where a radionuclide was added to a system solution/solid phase and its distribution in the system was analyzed as a function of time, of composition of the solid phase and of the solution, of the solid-to-solution ratio, and other factors. The results served for the modelling of the interaction of radionuclides or stable elements, with solids in the environment and for the analysis of the interaction mechanisms, including bonding of the radionuclides. One example of such an analysis concerning

the uptake of radium on suspended solids in river water has been shown in the previous paragraph [155]. Other examples are presented below as illustration of different modes of this approach.

Many authors studied the uptake and/or release of radionuclides by different model solids representing mineral or organic components of sediments, soils, or rocks, e.g., [156–159]. The differences among the solids were used for an assessment of the role of the corresponding components in the bonding of radionuclides in environmental solids. Some authors tried to predict quantitatively the uptake of trace elements by sediments from parameters deduced from model solids (components) [160, 161]. It has been shown, however, that, for instance, the adsorption affinity of river sediments for radium cannot be predicted accurately from their composition and other properties [162]. Therefore, reliable conclusions on the speciation of radionuclides are not easy to obtain from the experiments with model solids.

Another type of model experiments is based on laboratory studies of the uptake of radionuclides by environmental solids, as function of the composition, or of other properties of the solids or of a pre-treatment of the solids. For instance a study of the adsorption of ^{137}Cs on river sediments leached by the sequential procedure of Tessier *et al.* [117], revealed that ^{137}Cs was, as expected, mainly adsorbed on clay components [163]. A similar approach has been used earlier for the analysis of plutonium speciation in soils [164].

Other authors analyzed the speciation in model experiments, where an environmental solid was first labelled with a radionuclide, and then selectively leached [113, 165, 166]. Faure [165] combined this procedure with gel chromatography of the leachate. Davydov *et al.* [113] compared leaching of contaminated soils from the Chernobyl accident with leaching of the same, but artificially contaminated soils with ionic forms of radionuclides in the laboratory.

Model experiments can also be useful for the development and check of the selectivity of methods for direct experimental analysis of the speciation in environmental solids. For example, Spalding [167] added calcium carbonate, labelled by co-precipitation with ^{85}Sr , and studied the selectivity of leaching of carbonates from the soils with several reagents.

3. Speciation of airborne radionuclides

The atmosphere plays a very important role for the proliferation of radionuclides. Many of the natural and artificial radionuclides have entered the terrestrial environment via atmospheric fallout. On the other hand, radionuclides may re-enter into the atmosphere from land and sea by wind action, sea spray and diffusion.

3.1 Sources

The number of volatile and airborne radionuclides is limited. Radionuclides in the atmosphere result from different sources:

i) *Radon isotopes* (^{220}Rn , $T_{1/2}$ 56 s and ^{222}Rn , $T_{1/2}$ 3.8 days) and *decay products* (e.g., ^{210}Pb , ^{210}Bi , ^{210}Po). Radon, a noble gas, escapes from the earth's surface into the atmosphere. It is almost exclusively produced on continental land masses. One observes considerable local and temporal variations in the concentrations of radon and its decay products. The variability is related to climatic and weather conditions. If the observations are extended and averaged over yearly periods, the specific activities (e.g., in $\mu\text{Bq m}^{-3}$) of the decay products of radon become remarkably constant [168].

ii) *Interactions of cosmic radiation* in the upper atmosphere with N_2 , O_2 , and Ar. The production by cosmic radiation leads to constant steady-state concentrations of radionuclides. Examples for radionuclides formed by nuclear reactions are ^3H , ^7Be , ^{10}Be , ^{14}C , ^{26}Al , ^{32}Si , ^{36}Cl .

iii) *Nuclear weapons tests* in the atmosphere, mainly during the period 1950–1963, have produced vast amounts of ^3H , ^{14}C , fission products, unreacted ^{235}U , ^{239}Pu , neutron reaction products from the casing of the bombs (e.g., ^{55}Fe), and minor amounts of ^{210}Pb / ^{210}Po , and actinide elements. These products disappear from the atmosphere with on-going time by radioactive decay and by dry and wet fallout.

iv) *Uranium mining, installations of the nuclear fuel cycle, and nuclear reactors* release limited and controlled amounts of volatile radionuclides, e.g., ^3H , ^{14}C , ^{85}Kr , ^{129}I and ^{222}Rn , into the atmosphere. This leads to a slow, but continuous global increase of their atmospheric concentrations. Accidents in nuclear installations may locally enhance the radioactivity by release of aerosols. But they can, as in the case of the Chernobyl accident, contaminate the environment on a large, almost global scale. This accident has clearly demonstrated the importance of airborne radioactivity as one of the main pathways for the proliferation of radioactivity.

v) *Coal burning*. The burning of coal by industry and households releases considerable amounts of radioactivity into the atmosphere. Most of the emitted products belong to the uranium and thorium decay series. An extensive review article on radioactivity from coal-fired power plants was published [169].

vi) *Re-suspension* from soil and the sea by wind action [170]. Re-suspended aerosols can travel over very long distances as is well known and often seen by the appearance of desert dust in remote areas. The transfer of radionuclides from sea to land via the atmosphere was reviewed by [171]. Sukhoruchkin *et al.* [172] showed that contaminated soils in the Chernobyl area are resuspended by wind action and agricultural activities.

3.2 Speciation

i) *Radon and decay products*. Radon-222 results from α -decay of ^{226}Ra . After formation in soils and sedi-

ments, radon diffuses into the atmosphere where it decays. The decay products are single heavy metal atoms or ions which nucleate to molecular clusters with water, oxygen, and trace gases. The primary clusters attach quickly (near the earth's surface within minutes) to ubiquitous natural aerosols [173]. These particles and the "adsorbed" longer-lived decay products (^{210}Pb , ^{210}Bi , ^{210}Po) return to the earth's surface by wet and/or dry precipitation. Mean residence times of atmospheric aerosols (about 20–40 days) can be calculated from the $^{210}\text{Bi}/^{210}\text{Po}$ activity ratios [174]. Not much is known about the chemical forms of radionuclides in primary and secondary aerosols. A substantial fraction of the initial α -decay products are ions with a charge distribution from +9 to -2 [175]. Charge transfer processes with common atmospheric molecules rapidly lead to single charged states. These ions are likely to become associated with clusters of water vapour (5–8 molecules) or other atmospheric constituents (e.g., NH_3). Collisions of these clusters with aerosol particles lead to charge exchange and the formation of secondary radioactive particles [176]. Bondietti *et al.* [177], using impactors which collect particles in a certain size range, found ^{212}Pb and ^{214}Pb mostly on aerosols with sizes $<0.52 \mu\text{m}$. The sizes of aerosols carrying ^{210}Pb were somewhat larger in summer than in winter. The ^{210}Pb labelled aerosols grew by about a factor of two during their atmospheric lifetime. Hot atom chemistry determines many of the discussed initial phenomena. A review on hot atom chemistry was presented by Adloff *et al.* [178] in a recent handbook.

ii) *Cosmogenic radionuclides*. Tritium (^3H), ^7Be , ^{10}Be and ^{14}C result predominantly from nuclear reactions of cosmic radiation with atmospheric nitrogen and oxygen, ^{32}Si , ^{32}P , ^{35}S from spallation of atmospheric argon. The product atoms are initially highly excited atoms or ions [178]. Their subsequent transformation is not very clear. Probably they interact with photochemically excited molecules or highly reactive radicals of atmospheric oxygen or nitrogen [179]. Tritium and ^{14}C form gaseous products (^3HHO , ^3HH , $^3\text{HCH}_3$, $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$), and are distributed by the atmospheric cycles. For ^3H the relative concentrations found in the atmosphere are: $^3\text{HH} > ^3\text{HHO} >$ hydrocarbons [180]. Beryllium-7 and ^{10}Be may form BeO and sorb on aerosol particles. Phosphorus-32 and ^{35}S become oxidized and appear ultimately in the form of phosphates and sulphates [181]. Number, surface and volume concentrations of aerosols decrease rapidly with increasing altitude [182]. Due to very small aerosol concentrations, the life-times of the primary particles in the higher atmosphere are of the order of hours [173].

iii) *Radionuclides from nuclear tests*. The majority of the products formed in the atmosphere by nuclear bombs attach to debris-particles from the explosion. The particulate radioactivity has a wide size distribution. *Strontium-90* and ^{137}Cs are found among the

smaller particles, ^{95}Zr and ^{144}Ce are often related to larger-ones [173]. This difference is due to gaseous precursors (i.e., ^{90}Kr and ^{137}Xe) in the case of ^{90}Sr and ^{137}Cs [173]. Their formation from the precursors occurs after the fallout of larger particles from the explosion. *Tritium* appears as ^3HHO , ^{14}C as $^{14}\text{CO}_2$. The gaseous fission products remain unchanged and disappear by radioactive decay.

iv) *Products from nuclear installations.* During normal operation, the releases from nuclear facilities into the atmosphere are gaseous products i.e., ^3H , ^{85}Kr , ^{14}C , ^{129}I or ^{222}Rn . *Tritium* is released as ^3HH (hydrogen gas) and can be distinguished from ^3HHO (water) formed by cosmic rays and nuclear tests. *Carbon-14* escapes in the form of $^{14}\text{CO}_2$ [183]. Several papers by the group of Aumann, e.g., [184] were devoted to the release of *iodine* by a small nuclear fuel reprocessing plant, but the speciation was not indicated. Fuel processing and waste solidification installations may, in addition, release *ruthenium*, *caesium* and *technetium* [185]. According to these authors the primary product of ruthenium is RuO_4 which is rapidly decomposed to solid RuO_2 or to condensed $\text{Ru}(\text{NO})$ compounds in liquid condensates, and caesium and technetium may form common compounds such as CsTcO_4 .

This situation contrasts sharply to that of accidents, when large amounts and a variety of radioactive species can escape uncontrolled into the environment. The most drastic example of such a release was the *Reactor Accident at Chernobyl* (e.g., [186]). Radioactive gases and aerosols reached altitudes > 1200 m and were dissipated over large areas of Europe. Later, products of this accident were also detected in more remote places of the globe, demonstrating the importance of airborne proliferation. At distances $< 15\text{--}30$ km from the damaged reactor, the composition of the radioactive fallout approached that of the reactor fuel. Plutonium, Sr and other non-volatile radionuclides were mainly found in primary fuel particles.

"Hot particles" (HP, i.e., particles carrying a high radioactivity) were among the forms of release from the damaged Chernobyl reactor. An excellent review article on HP was recently published by Sandalls *et al.* [187]. The fallout of HP occurred mainly in the zone close to the reactor, but was also detected after long transport distances, e.g., [188]. One could distinguish two major forms of HP:

– Relatively large fragments of the fuel matrix itself with diameters of tens of μm . They contained radioisotopes of *Ba*, *Ce*, *Zr*, *Nb*, etc., but were depleted in *Cs* and *Ru*. The nuclear composition of a HP and a comparison to the composition of reactor fuel is shown in Table 4. About 10% of the large HP were '*ruthenium particles*' containing high activities of ^{103}Ru and ^{106}Ru . In parts of the reactor, a chemical reaction with CO (from burning graphite) to form metallic ruthenium might have occurred. This process could be the source of the '*hot ruthenium particles*' [186]. In other parts of the reactor, fission-ruthenium was prob-

Table 4. Nuclear composition of a 'hot particle' (HP), released on 6 May 1986 from the damaged Chernobyl reactor. For comparison, the composition of the associated reactor fuel is shown [189]

| Nuclide | 'Hot particle' (%) | Reactor fuel after three years of operation (%) |
|------------------------------|-----------------------|--|
| ^{95}Zr | 17.9 | 17.6 |
| ^{95}Nb | 20.7 | 19.3 |
| ^{103}Ru | 14.2 | 15.0 |
| $^{106}\text{Ru}(\text{Rh})$ | 3.5 | 2.4 |
| ^{131}I | – | 4.0 |
| ^{134}Cs | – | 0.6 |
| ^{137}Cs | – | 1.2 |
| $^{140}\text{Ba}(\text{La})$ | 12.6 | 11.1 |
| ^{141}Ce | 15.8 | 14.3 |
| $^{144}\text{Ce}(\text{Pr})$ | 15.8 | 14.4 |

ably oxidized to volatile RuO_3 or RuO_4 by air entering the damaged reactor. These very volatile Ru-oxides were able to travel over long distances and contributed to a major part of the fallout radioactivity.

– *Smaller HP* (diameter several μm) with a very variable composition. HP found outside the former USSR belonged to this second group. The radioactivity of individual HP of both classes covered a wide range from tens to thousands of Bq.

Not much is known about the *chemical forms of ^{134}Cs and ^{137}Cs* from Chernobyl in the atmosphere. A possible form could be CsTcO_4 , like in fuel processing plants [185]. This would then also explain the presence of $^{99\text{m}}\text{Tc}$ among the Chernobyl activity in the fallout in Switzerland in May 1986 [190]. Results of Hilton *et al.* [191] showed that 70% of the ^{137}Cs in Chernobyl fallout was water-soluble. This result agrees with observations of the research group of one of the present authors [192], but contrasts with recent data of Rybáček *et al.* [193], who found during 1986–1992 in fallout samples from Prague, about 70% of the deposited Cs in a water insoluble form. A possible explanation of this discrepancy might be that the samples collected in Prague contained more Cs in particulate form than the fallout recovered at larger distances from the damaged reactor. Al Rayyes *et al.* [194] demonstrated in laboratory experiments that Cs may be sorbed strongly to uranium oxide aerosols under conditions which occurred during the Chernobyl accident. Bondietti *et al.* [195] measured the growth rate of Chernobyl aerosols in the lower troposphere to be $0.013 \mu\text{m}$ per day for particles of about $0.4 \mu\text{m}$ diameter.

The fate of ^{131}I from the Chernobyl reactor was investigated by several authors. Jost *et al.* [196] postulated that ^{131}I in the atmosphere was mainly present as a gas of unknown composition, and was removed by rain. This postulate was deduced from the particle size distribution of Chernobyl- ^{131}I which deviated significantly from that of other aerosols. In agreement with this result, Uematsu *et al.* [197] found a gas-to-particle conversion time for ^{131}I in the atmosphere of 2–3

Table 5. Distribution of radio-iodine species in the atmosphere after the Chernobyl accident. Comparison with results from the Three Mile Island accident [after 199]. 'Organic' indicates CH₃ and higher alkyl iodides

| Location | Species distribution % | | |
|--|------------------------|-----------|---------|
| | Aerosol | Inorganic | Organic |
| Sweden 30.4.–2.5.1986 | 20–25 | 75–80 | |
| Hungary 30.4.–9.5.1986 | 30 | 70 | |
| CSFR - Crnava 1.5.–7.5.1986 | 26 | 36 | 38 |
| CSFR - Prague 1.5.–9.5.1986 | 24 | 33 | 43 |
| Japan 5.5.–10.5.1986 | 30–35 | 65–70 | |
| Three Mile Island ¹ 1979 | 50–75 | | 25–50 |

¹ Referred to TMI reactor accident.

weeks. The Chernobyl size distribution for ¹³¹I in the atmosphere was similar to those of ¹²⁷I and ¹²⁹I [198]. Tomášek *et al.* [199] measured the speciation of Chernobyl fallout in the former Czechoslovakia and compared it to that at other locations (Table 5).

Their results are similar to those of others (e.g., [188]) and also not too different from samples of airborne ¹³¹I in Japan (19% particular, 11% inorganic, 70% organic; [200]). The importance of organic iodides (e.g., CH₃I) for the volatilisation of ¹³¹I in reactor accidents was demonstrated by Wren *et al.* [201]. In summary, these investigations showed that CH₃I is a ubiquitous component of iodine in air. It is probably also the primary form in which iodine is released from oceans and vegetation [202].

The discussions from above demonstrate that speciation of radionuclides in the atmosphere is strongly dependent on source, mechanisms of production and environment. The radionuclides in the atmosphere are either gaseous products, or are attached to small particles. For most of the particulate radioactivity not much is known about speciation of the radionuclide itself.

The *removal* of the radioactivity from the atmosphere occurs mainly by *radioactive decay* of the noble gases and ³HH, by *radioactive decay and wet precipitation* for ³HHO, ¹⁴CO₂, ¹⁴CH₄, I₂, and CH₃I, and by *radioactive decay, and dry and/or wet fallout* for particle-bound radioactivity. The removal rates depend on the intensity of wet precipitation and on particle sizes. Livens *et al.* [203] indicated *wet* deposition as the main process for fallout of ¹⁰³Ru and caesium isotopes, whilst *dry* deposition was most important for ¹³¹I. In dry fallout, deposition velocities of the order of 0.2 to 2 mm s⁻¹ were estimated for particles in the size range 0.1 to 2 μm [204] and for ¹³¹I in a size range of 3–4 μm [203]. These authors [204] also indicated that re-suspension can redistribute radionuclides over large

distances. Re-distribution depends mainly on wind speed and particle sizes.

4. Speciation of radionuclides in the hydrosphere

The speciation of radionuclides in the hydrosphere depends on their chemical nature, on sources and on the composition of the water. As the composition of waters in different parts of the hydrosphere varies considerably and radionuclides originate from many sources, significant differences can be found among the speciation of radionuclides in various water bodies.

4.1 Groundwaters

An extensive review article of calculated, thermodynamically stable species of radionuclides in groundwaters was published by Rai and Serne [11]. Groundwaters contain mainly *natural radionuclides* released from rocks by dissolution, desorption, erosion or atomic recoil by radioactive decay. The release depends on the solubility of the host rock and on the bonding of the radionuclide. Radionuclides are usually released as dissolved species but a release as particles or colloids is also possible. Dissolved forms may be converted to particulate or colloidal forms by adsorption or (co)precipitation. *Uranium, radium and ⁴⁰K*, which form soluble compounds, are released predominantly as dissolved species. The simple cation K⁺ prevails among ⁴⁰K species. Uranium is often present in groundwaters as (UO₂)²⁺ ion or as carbonate or phosphate complexes of hexavalent uranium [205]. However, some groundwaters contain tetravalent uranium [206]. A relatively high mobility of *uranium* was found in the Glattfelden aquifer (Switzerland). Here, significantly higher summer concentrations of uranium in the River Glatt could be used for an estimation of the migration behaviour of uranium in the interconnected glacio-fluvial aquifer. An *in-situ* K_d value for uranium of 10 ml g⁻¹ was deduced from its retarded movement relative to the groundwater [207, 208]. Using Chelex-100® or Bio-Beads SM-16® resins, it was demonstrated that uranium was predominantly present as the UO₂(CO₃)₃⁴⁻-complex [207, 208]. *Uranyl-humate* interactions were investigated in soft acidic waters [209]. These authors were able to determine an overall log conditional stability constant of 6.5 ± 0.8 for uranium concentrations of 5 × 10⁻⁸ M to 2 × 10⁻⁷ M in the presence of 3.5 mg L⁻¹ Aldrich® humic acid. Under anoxic conditions microbial activity seems to immobilize uranium [210]; we assume that this is probably due to reduction to the +4 state.

Radium is most frequently found as Ra²⁺ cation, but it can also form a RaSO₄ complex or carbonate complexes in alkaline groundwaters containing higher concentrations of free CO₃²⁻ [211]. Particulate forms of radium were also reported [212]. *Lead-210* is more prone to formation of complexes like PbCO₃. PbOH⁺ or PbCl⁺ and to adsorption on or co-precipitation with

colloidal particles in groundwaters [213]. Strong hydrolysis of *thorium* and *polonium*, and the extremely low solubility of their oxides/hydroxides are the reason why ^{232}Th , ^{230}Th and ^{210}Po migrate in groundwaters mainly in colloidal forms [214–216].

Underground repositories of radioactive wastes and the transport of radionuclides from contaminated soils or surface waters may represent significant sources of *artificial radionuclides* in groundwaters. Release and migration of radionuclides from nuclear wastes strongly depend on their chemical composition and on the speciation of the released radionuclides. It is well known that cationic radionuclides like $^{137}\text{Cs}^+$, Ra^{2+} , etc., are strongly retarded by the solid phase of an aquifer or soil due to adsorption or co-precipitation. Ion exchange may be another possibility for retention of these two ions. Neutral or anionic forms are usually more mobile in groundwaters. These forms are either simple anions like $^{131}\text{I}^-$ or inorganic and organic complexes [11, 217]. Nitsche *et al.* [218] showed that *Am* forms hydroxy-carbonates in carbonate-rich water.

Of particular importance is *complex formation* with strongly complexing *organic ligands* (e.g., NTA, EDTA, citric acid, etc.) present in wastes [63, 70, 219] or with natural organic matter (i.e., fulvic and humic acids) eluted from soils ([151, 154, 220], see also Chapter 5). A review on complex formation of humic substances with *actinides* (*Th*, *U*, *Np*, *Pu*, *Am*, *Cu*) and with important cations in natural waters was recently published by Moulin *et al.* [16]. These authors presented calculated speciation diagrams for natural system conditions (pH 4–9, and 0.1 to 10 ppm humic substances). Humic substances dominated actinide (*Th*, *U*, *Am*) speciation up to pH 7 or 8. Above this pH, inorganic complexes regulated actinide speciation. The presence of competing cations (*Ca*, *Al*) modified actinide speciation in the pH range 4–6.

Significant complexation with organic ligands in groundwaters was determined for ^{60}Co [12, 63, 151, 154, 219], ^{90}Sr [221], ^{137}Cs [221], ^{238}Pu [70]. Olsen *et al.* [222] analysed the release of radionuclides from a liquid waste disposal trench of the Oak Ridge National Laboratory. They found a considerable mobility for ^{99}Tc , ^{60}Co and ^{233}U which they attributed to low molecular weight anionic complexing. Another plausible explanation could be based on batch laboratory experiments by Grütter *et al.* [223], who found, with selected size fraction of clay minerals and glaciofluvial sediments, that the sorption kinetics of cobalt and nickel is very slow. In contrast, the concentrations of ^{90}Sr and ^{137}Cs were extremely low in the groundwater due to an artificial alkaline environment near the trench which enhanced sorption and precipitation of ^{90}Sr , and the strong and selective sorption of ^{137}Cs to illite. This result agrees with those of [224, 225].

The existence of *colloidal forms* of some radionuclides may significantly affect radionuclide transport in groundwaters. Colloids may be released from nuclear wastes, or may be formed by precipitation of sparingly soluble compounds of radionuclides and by

association of radionuclides with inorganic or organic colloids ('Fremdkolloide', [226, 227]) present in groundwaters [214, 228–230]. Colloidal forms of ^{60}Co , $^{152,154,155}\text{Eu}$ and ^{144}Ce were found to predominate in groundwaters of the Nevada Test Site [56]. Kim *et al.* [231] were able to show that *U(VI)*, *Am(III)*, *Cm(III)*, and *Th* were strongly sorbed to aquatic colloids, rich in humic and fulvic substances, whereas *Np(V)* was negligibly sorbed to these colloids.

Oxidation or reduction processes play an important role in groundwaters, because the solubility and the adsorption behaviour of different oxidation states of radionuclides differ considerably [232, 233]. It is well known that, for instance, a reduction of uranium to +4 state leads to formation of uranium colloids [234]. Tan *et al.* [235] found that plutonium (V and VI) may be reduced by humic acids to the +3 and +4 state. Redox equilibrium, possibly influenced by organic substances, also affected the transport of ^{99}Tc and ^{60}Co in shallow groundwaters [236, 237]. Reviews, concerning the chemical behaviour of *transuranic elements* in natural aquatic systems, have recently been given by Kim [78], and Dozol and Hagemann [238]. Due to the completeness of these reviews, the treatment in the present paper can be restricted to the most relevant facts.

The contamination of groundwaters by radionuclides from surface waters and soils depends also on the speciation of radionuclides in these two compartments (see below and Chapter 5). The fallout from the reactor accident at *Chernobyl* was used to investigate the migration of radionuclides which had *infiltrated from a river* into a shallow, well characterized aquifer at *Glattfelden, Switzerland* [190, 192]. These studies showed that ^{131}I , and ^{103}Ru moved in the aquifer without retardation. *Iodine* was found predominantly as I^- (90%), and IO_3^- (10%), *ruthenium* probably as perruthenate ion. *Tellurium-132* was slightly retarded in the aquifer and might have been present as tellurate ion. The *caesium isotopes 134 and 137* did not infiltrate, but were, as expected from the results of [224], completely sorbed by the aquifer materials. It was, furthermore, demonstrated that colloidal transport of radionuclides was not important for radionuclide migration in this calcite-rich aquifer. Groundwaters in calcite environments have an ionic strength of about 10^{-2} M which favours coagulation of colloids and their subsequent mechanical filtration in the heterogeneous aquifer. Furthermore, coagulation of colloids may have been enhanced by a decrease of the pH (8.3 \rightarrow 7.5) at the river/groundwater interface due to the oxidation of organic matter.

4.2 Surface waters

receive radionuclides from *springs* (groundwaters), from *atmospheric precipitation*, from *leaching or erosion of solids* (soils, sediments) and from the discharge of *waste waters*. Concentration and speciation of ra-

dionuclides in these sources may be very variable. The speciation of radionuclides in surface waters usually undergoes significant changes caused by a number of processes such as hydrolysis, complex formation, precipitation, co-precipitation, adsorption, desorption etc. The processes are described in general reviews for trace components of water, e.g., [32, 239, 240, 241]. A characteristic feature is the very low concentration of reactants especially for carrier-free radionuclides.

If an element consists of *radioactive and stable isotopes*, the radioisotopes usually follow in speciation and behaviour the more abundant stable isotopes. Isotope exchange is an important process affecting speciation of radionuclides. However, rather large differences in the speciation are sometimes found between radioactive and stable isotopes, particularly if the radionuclide is short-lived. This is caused by slow isotopic exchange kinetics, especially if radioactive or stable isotope(s) form inert complexes or are incorporated into solid phases. The decay of a radionuclide will seldom influence its speciation [32] except for members of natural or artificial decay chains which are found in specific forms after formation by decay. This effect has usually to do with recoiling atoms translocated into the solid phase, i.e., with colloidal or particulate forms. In some cases a high specific alpha activity of solid ('hot') particles can affect their properties due to radiolysis.

Among the most important characteristics of radionuclides in surface waters are their distributions among *particulate, colloidal and truly dissolved forms* (operationally defined as >450 nm, 1–450 nm and <1 nm, respectively), sometimes called the "physical speciation". This distribution primarily affects *transport and biological availability* of a radionuclide and its deposition to sediments. It exhibits pronounced differences among different water bodies. The largest proportion of particulate forms is usually found in rivers, especially under high flow conditions. A pronounced increase in the abundances of the particulate forms with increasing flow rate was reported, e.g., for ^{137}Cs [242]. Inorganic (mineral) particles prevail as carriers for radionuclides in rivers.

The concentrations and properties of particulate and colloidal forms of radionuclides undergo large changes in *estuaries* due to coagulation, sedimentation, and desorption. These changes are caused by an increasing or decreasing salinity of the water and by changing hydrodynamic conditions. They are reflected for instance in the decrease in concentration of particulate forms of ^{137}Cs in an estuary with increasing salinity of the water [51, 243]. Freshwater reservoirs and particularly the sea generally contain a much lower proportion of particulate radionuclides due to efficient removal by sedimentation. For instance, ^{210}Pb and ^{210}Po are present in *seawater* mainly in forms passing through a 400-nm membrane filter [244], whereas particles larger than 400-nm prevail in *rivers* [52]. A significant proportion of colloidal forms was reported for ^{210}Pb in *lake water* [245], for *Pu* in an *estuary water*

[51] and for *uranium in seawater* [246]. Participation of living or dead organisms in the formation of particulate forms of radionuclides increases in the order: *rivers < reservoirs < sea*.

The distribution among particulate, colloidal and dissolved forms depends on the chemical nature of radionuclides due to differences in their solubility and affinity for the carrying solid phase. Surface charges of particles, ions and complexes play also an important role. Early results illustrated that ^{51}Cr and ^{124}Sb migrated in the *Columbia River* predominantly as dissolved species (in average about 95%), whereas the average fractions of dissolved ^{46}Sc , ^{54}Mn , ^{58}Co , ^{59}Fe , ^{60}Co and ^{65}Zn were generally much lower and depended on the radionuclide [247]. Some authors estimated the distribution among different phases using equilibrium or kinetic models with participation of solids in speciation or transport calculations, applying mathematical terms for solubility equilibrium or adsorption/desorption processes, e.g., [158, 248]. However, limited success was achieved due to the complexity of the systems.

An experimental analysis of the distributions among different phases in a specific system is indispensable, if reliable conclusions are to be drawn. The analysis should also characterize the particulate or colloidal forms, and especially the character of the bond of a radionuclide. Such an analysis can elucidate the source of the radionuclide, mechanism of formation of the species and probable behaviour of a radionuclide in the system [249]. Sequential leaching of particulate solids of a river has shown that ^{60}Co was mainly bound to *Fe/Mn oxides* whereas the majority of ^{137}Cs was associated with the *clay fraction* of the solids [243].

Variable compositions of surface waters exert pronounced effects also on dissolved forms ('chemical speciation') of radionuclides. This is mainly due to different extents of complexation with inorganic and organic ligands. For instance, the higher concentration of chloride and sulphate in seawater, as compared to freshwater, can result in a larger abundance of chloride and sulphate complexes [250], while the complexation of radionuclides with carbonates and organic ligands should be higher in freshwaters.

4.3 Aquatic sediments

A major fraction of radionuclides entering the hydrosphere becomes associated with *bottom sediments* of freshwater, estuary or seawater systems. Radionuclides tend to accumulate in suspended or bottom sediments by precipitation or co-precipitation (limited solubility), by adsorption, biological uptake and by sedimentation of particles (inorganic or organic, living or dead) present in water. Bottom sediments are either a permanent sink of radionuclides, which are transferred from the hydrosphere to the lithosphere by diagenetic processes, or a temporary reservoir, if the radionuclides are again released into the water column in dissolved or particu-

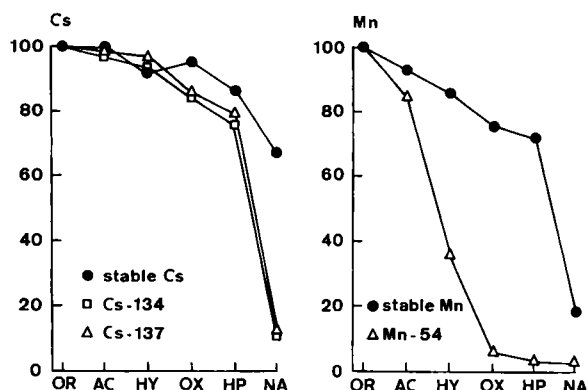


Fig. 4. Extraction curves for stable caesium, ^{134}Cs , ^{137}Cs , stable manganese and ^{54}Mn in sediment samples from the lower Rhone River. Original sediment (OR) and percentages remaining after acetate (AC), hydroxylamine (HY), oxalate (OX), hydrogen peroxide (HP) and nitric acid (NA) extraction [from 251].

late (re-suspended sediment) forms. The release from sediments can become a major source of radionuclides in a water body, particularly if other sources diminished or ceased to exist.

The release of radionuclides from sediments is of environmental concern. It depends not only on the hydrologic conditions at a given water body but also on the speciation (bond) of the radionuclides in the sediment. The speciation can substantially affect the bioavailability of radionuclides for bottom feeding organisms and the environmental behaviour of radionuclides if contaminated sediment is deposited on soil. These are main reasons why the speciation of radionuclides in sediments has to be studied. A further reason for such studies is the fact that the knowledge of speciation may contribute to a characterization of sources of radioactive pollution for the corresponding water body. Bottom sediments conserve a record of the pollution as the distribution of radionuclides (and other pollutants) in a vertical sediment profile reflects the accumulation history. The speciation of radionuclides in sediments depends on their primary form in the source, on the mechanisms of accumulation and on the chemical conditions within the sediments. Consequently, studies on the speciation of radionuclides in sediments have been aimed at the elucidation of sources of pollution, on the mechanisms of accumulation of the contamination and at the prediction of the further behaviour of radionuclides in environmental processes.

Several studies have shown that the occurrence and extent of radioactive contamination of sediments can be assessed not only from the concentrations of radionuclides in sediments but also from an analysis of the character of the binding strength of radionuclides. First, polluting radionuclides are often bound less firmly to sediments than their stable natural isotopes. This reflects different accumulation processes, different reactions with solid phases, and different residence times [251, 252]. This is illustrated in Fig. 4, where the $^{134,137}\text{Cs}$ and ^{54}Mn content in Rhone River sediments

Table 6. Distribution of ^{226}Ra (in %) in river sediments among forms determined by sequential extraction with 0.1 M NaCl ('loosely bound', LB), 1 M HCl ('acid soluble', AS) and hot alkaline 0.1 M EDTA (BaSO_4 form). 'Residue' remaining after the extractions [104]

| Distance from the source (in km) | Form | | | |
|----------------------------------|------|------|-----------------|---------|
| | LB | AS | BaSO_4 | Residue |
| -1* | 1.1 | 51.3 | 34.7 | 12.9 |
| 0** | 0.1 | 1.7 | 92.0 | 6.2 |
| 1 | 0.9 | 18.5 | 70.9 | 9.7 |
| 5 | 0.8 | 11.2 | 82.5 | 5.5 |
| 45 | 4.9 | 41.9 | 39.1 | 14.1 |

* River sediment above the discharge point.

** Sediment from the waste water source.

decreases more rapidly in a series of sequential extractions than the stable elements. Second, the distribution of radionuclides among phases or binding sites in polluted sediments can be significantly different from the distribution of the same radionuclides, naturally present in a non-polluted sediment. For instance the analysis of the binding of ^{226}Ra and ^{210}Pb in sediments contaminated from uranium mining revealed that about 80% of the radionuclides were 'non-residual' ('non-detrital'), i.e., could be extracted with 0.5 M HCl [253]. The non-residual fraction of the same radionuclides in uncontaminated, 'background' samples was only 38–45%.

Detailed studies of radium bonding in suspended solids [249] and bottom sediments [97, 104] showed that surface waters, downstream of uranium mining/milling installations, were often contaminated with radium in barium sulphate. The presence of radium in sediments indicated an escape of barium sulphate from the water purification process and could be used for an identification of the source of the contamination.

Table 6 shows differences in speciation of radium in river sediments resulting from purified waste waters of a uranium mine at various distances downstream from the point of discharge, and in the uncontaminated river upstream of the discharge. Another example of the applicability of the speciation for a similar purpose was given by Plater *et al.* [111] who used a sequential extraction procedure in combination with the determination of uranium and thorium isotopic ratios for elucidation of the transfer of uranium and thorium from weathering processes to river sediments.

The differences in the ratio of nonresidual to residual forms of radionuclides reflect the main differences among the mechanisms of contamination of sediments with radionuclides: adsorption or co-precipitation vs. release of detrital particles containing radionuclides incorporated into acid-resistant minerals. For instance, a rather low abundance (<30%) of residual forms of ^{210}Pb and ^{226}Ra bound in stream sediments of the Northern Territory, Australia, indicated that the sediments were contaminated mainly by adsorption of dissolved radionuclides from a spring of

high natural radioactivity [105]. Similarities or differences in an extraction of ^{226}Ra and ^{228}Ra from *stream sediments* were used as evidence that the radionuclides were adsorbed in the same [106], or in different [254] forms in the sediments.

A more comprehensive analysis of the mechanisms requires, however, a determination of the phases with which the radionuclides are associated. Analyses by various procedures of the sequential extraction have commonly indicated multiphase associations. The distribution of a radionuclide among different phases depends on the chemical nature of the radionuclide and may also depend on the type of sediment. Many radionuclides tend to be predominantly associated with *Fe/Mn(hydr)oxides*, frequently present in sediments as surface coatings or (less abundant) distinct crystals: ^7Be [243], ^{54}Mn [252], $^{58,60}\text{Co}$ [243, 255], ^{65}Zn [243], ^{210}Pb [243, 253], $^{239,240}\text{Pu}$ [256, 257]. Less often prevails the association with organic components (^{239}Pu , [122]), or carbonate minerals (*Ra*, [253]). *Thorium* is typically present in residual forms [111].

A significant part of some radionuclides interacts by ion exchange, by electrostatic adsorption or surface complexation on clay and other components of sediments: e.g., ^{137}Cs [255], ^{144}Ce [103], ^{226}Ra [97, 253]. Three kinds of bonds can experimentally be distinguished for ^{137}Cs on *clay* components [102]: i) caesium bonds to sites at planar clay surfaces, ii) to wedge sites and iii) to interlayer sites. The bonds differ in exchangeability of caesium against various ions and, consequently, in the availability of radio-caesium for release from sediments. A major part of *radio-caesium* is bound so strongly to interlayer sites that it is mainly found in the residues of the leaching procedures [102, 103, 252, 255], although it can sometimes be leached with 50% NH_4NO_3 [125]. Caesium probably exchanges against NH_4^+ which has a relatively similar ionic radius.

Large variations in the speciation are found among different sediments. For instance, ^{137}Cs [103, 115] and ^{144}Ce [252] are bound differently in *river and seawater sediments*. As the strength of bonding of caesium depends on the content of clay minerals in sediments [102], a smaller strength may reflect a lower content of clay minerals in seawater sediments. The size of sediment particles can also play a significant role. An increase in the concentrations of radionuclides in sediment fractions with decreasing grain sizes can be considered as an indication of adsorption as the main mechanism of sediment contamination [120, 123, 125]. Schoer and Foerstner reported [252] that the extractable portion of $^{134,137}\text{Cs}$ in separated size fractions of river and seawater sediments decreased with decreasing grain size and explained this fact by a change in clay content of the fractions. For radio-caesium it was observed that the strength of its bonding increased with the time elapsed since the contamination of the sediment [243, 255]. This can be used to distinguish between *fallout- ^{137}Cs* and ^{137}Cs released from nuclear power plants.

Table 7. Correlation coefficients (r) between radionuclide concentrations in soft tissues of clams feeding on labelled sediments and radionuclide concentrations removed from these sediments by chemical extractants [according to 157]

| Extractant | $^{110\text{m}}\text{Ag}$ | ^{109}Cd | ^{60}Co | ^{65}Zn |
|--|---------------------------|-------------------|------------------|------------------|
| None (total radionuclide) | 0.936 | 0.022 | 0.173 | 0.228 |
| NH_4Ac | 0.077 | 0.744 | 0.788 | 0.947 |
| EDTA + NaOH | 0.812 | 0.534 | 0.683 | 0.752 |
| EtOH | 0.903 | 0.993 | 0.793 | 0.551 |
| HCl | 0.651 | 0.071 | 0.401 | 0.328 |
| HAc | 0.327 | 0.383 | 0.400 | 0.317 |
| $\text{H}_2\text{O}_2 + \text{C}_6\text{H}_8\text{O}_7$ | 0.637 | 0.389 | 0.257 | 0.352 |
| $\text{NH}_2\text{OH} \cdot \text{HCl}$ | 0.752 | 0.006 | 0.089 | 0.570 |
| $\text{Na}_2\text{S}_2\text{O}_4 + \text{C}_6\text{H}_8\text{O}_7$ | 0.965 | 0.055 | 0.374 | 0.007 |

Analysis of the availability of radionuclides in sediments for bottom-feeding organisms or for further physico-chemical transport in the environment was performed by simple extractions [102, 106, 157, 258] or by sequential extractions [102, 104, 251, 255, 257]. Luoma and Jenne [157] compared extractability of $^{110\text{m}}\text{Ag}$, ^{109}Cd , ^{60}Co , and ^{65}Zn , added to 6 different types of sediments, with the availability of the radionuclides for *deposit-feeding clams*, determined from the uptake of the radionuclides by the clams in the laboratory. Although significant correlations between some of the simple extractions used and the availability were found, none of the extractions quantitatively simulated the availability of all the radionuclides (Table 7). The same authors [259] reported that the differences in the uptake for the different sediments correlated well with the equilibrium sediment-water distribution coefficients for $^{110\text{m}}\text{Ag}$, ^{60}Co and ^{65}Zn . This suggested that the strength of metal binding to different sediments controlled the availability of the radionuclides to the clams.

When considering redissolution of radionuclides from sediments, the exchangeable forms of radionuclides determined by sequential extraction procedures are usually taken into account. Sometimes, however, other forms have also been considered [106, 243]. Evans *et al.* [102] attributed the mobilization of ^{137}Cs from bottom sediments of two small reservoirs during summer stratification to ion exchange of ^{137}Cs from two kinds of sites in clay minerals by cations released under anaerobic conditions. The mobilization of radionuclides may also be affected by changes of other environmental parameters such as pH, salinity and the concentration of complexing ligands [251]. A more quantitative prediction of the mobilization requires thorough studies of the effects of environmental parameters (e.g., [260]).

5. Speciation of radionuclides in the lithosphere

The top of the lithosphere consists in general of a soil layer. The speciation of radionuclides in the soil compartment is of prime importance, because radio-

nuclides may be taken up from here by living organisms. Due to this close interaction of the soil compartment with the biosphere, the main discussion in Chapter 5 is devoted to radionuclide speciation in soils. For a better understanding of radionuclide speciation and behaviour in soils we give a short discussion of soil properties. Excellent accounts on general soil chemistry are given by Bohn *et al.* [261], and Sposito [262]. Most of the principles described in these books can be applied to the chemical behaviour of radionuclides.

5.1 Soil

is the ultimate product of weathering. It is a very complicated mixture of *inorganic* and *organic solids*, *air*, *water* and (*micro*)*organisms*. The chemistry of radionuclides in soils is strongly influenced by the large surface area of very fine particles and colloids, the latter with sizes of 1–450 nm. Clay minerals (hydrous aluminium silicates, [263]), hydrous oxides (e.g., Fe(OH)₃), and polymeric organic substances (decay products of living organic matter) are the most important constituents which interact with compounds (e.g., radionuclides) in the soil solution. Colloidal and particulate organic matter is often sorbed, or chemically bound, to inorganic surfaces, or to biota and biological debris. Colloid stability is strongly influenced by ionic strength and pH, and changes of these properties. Clay minerals influence, together with hydrous oxides of Al, Fe, Mn and Ti, significantly the behaviour of many radionuclides in soils. Their adsorption to these compounds occurs by electrostatic forces, e.g., [264], surface complexation [28], and/or ion exchange.

Organic compounds consist of plant and animal residues at various stages of decomposition, and living soil organisms. The concentrations of organic compounds are usually much smaller than the inorganic part, but may alter soil properties significantly. The organic matter content of surface soils is usually only about 0.5 to 5% by weight. The concentrations of organic matter decrease from surface soils to deeper locations. Organic matter is subjected to a constant attack by soil (micro)organisms; much of it is in a rather transitory state and is constantly renewed by addition of plant residues. The degradation products of plants and animals undergo enzymatic and chemical reactions to form humus, a colloidal polymeric phase. Microbiology can drastically alter the soil environment, i.e., pH and Eh and may have a profound influence on water chemistry and on the speciation of radionuclides [10]. Due to the temperature dependent kinetics of micro-biological mediation, many processes occur in seasonal cycles and can influence speciation (e.g., [265]).

The composition of soil *humus* is very complex, incompletely known, and dependent on its origin and location. Humic substances are polyelectrolytes containing mainly carboxylic and phenolic OH-groups which enable complexation with a rather broad range

of elements [266] and radionuclides. In general, the concentrations and stability constants of these soil and water constituents are poorly known, and predictions about complexation are very difficult to perform. A review article on the coordination chemistry of humic substances was published by Grauer [267]. Sparkes *et al.* [268] made a literature survey of the organic speciation of radionuclides, and Grenthe [269] discussed competitive complex formation of radionuclides with humic and fulvic acids.

The presence or absence of a mobile interstitial water phase is a very significant factor for speciation and migration of radionuclides. The amount of pore water and interstitial water in the *unsaturated top soil* is regulated by climatic conditions, i.e., precipitation, temperature and atmospheric pressure. In the unsaturated top soil investigations involving the water phase are difficult to perform.

Deeper and saturated aquifers (groundwater, see also Chapter 4, Hydrosphere) contain usually much lower concentrations of organic matter than surface soils, and micro-biological activities are reduced due to limitation of nutrients. Contrary to the aerated *surface soils* and *unsaturated aquifers*, *deeper geologic formations* are often highly anoxic. These facts influence speciation and behaviour of radionuclides in this compartment. Therefore, one should bear in mind that the chemical differences between surface soils and the deeper saturated aquifers may lead to drastic speciation changes of radionuclides when they move from a repository of nuclear wastes in a deep geologic formation towards the earth's surface.

5.2 Sources

Primary and secondary *minerals* are the main sources for *natural radionuclides*, i.e., ^{235,238}U, ²³²Th and their decay products, and ⁴⁰K and ⁸⁷Rb. The distribution of natural radionuclides in the lithosphere is, in general, quite uniform on a macroscale, but may vary considerably in the microscale, and in ore deposits. The processes responsible for the release of *radionuclides* from minerals and soil constituents are closely related to those of *trace elements* and useful information can be found in publications related to this topic, for instance, in the book '*Applied Soil Trace Elements*' edited by Davies [270]. However, the releases of radionuclides may be enhanced by the effects of radioactive recoil processes [271]. Dry and wet precipitation (fallout) from the atmosphere (see Chapter 3) is the main source for the global distribution of *artificial and cosmic ray produced radionuclides* in the lithosphere.

On a local scale, the distribution of radionuclides in the lithosphere may be modified by the presence of ore bodies, by inputs from mining operations, by the nuclear industry, and by waste products from industrial, medical and research applications of radionuclides. The local additions occur in many different physico-

chemical forms. Furthermore, the primary distribution of radionuclides may be changed in the top soils by human activities such as agriculture and environmental changes [272].

5.3 Speciation

Ion exchange capacity, pH, redox conditions and complexation with humic substances determine speciation, behaviour and availability of radionuclides for the uptake by plants. A 'Critical Review of Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems' has been published by Coughtrey *et al.* [273–276]. These authors discuss in a very thorough and extensive manner, general principles, and treat the behaviour of the most important natural and artificial radionuclides separately. Once in the soil, further reactions can occur as the radionuclides equilibrate with the environment. These processes include immobilization by ion exchange, and precipitation and remobilization by complexing and dissolution [272]. One should bear in mind that the lithosphere, and especially soils, are not static systems. Due to their dynamics which are based on natural and man-made, physical, chemical, and biological processes, speciation may undergo significant changes with time. Examples (^{85}Sr ; ^{134}Cs , ^{110m}Ag) for this effect were given by Vidal *et al.* [277]. A discussion on effects of agriculture and fertilizers on the behaviour of radionuclides was presented by Desmet *et al.* [278].

Investigations by Cataldo *et al.* [279] demonstrated that plant processes may have a dynamic influence on chemical conditions in the soil. Polyvalent cations like *Al, Fe, Mn, Zn, Pu, Ni and Cd* may form highly mobile complexes with amino acids, peptides and organic acids originating from plant leaf litter and roots. The production of complexing agents was related to annual seasons and plant species. Unfortunately, as indicated above, not much is known about the stability constants of these complexes.

5.3.1 Specific radionuclides

Schell *et al.* [280] investigated several radionuclides in *forest soils* and *bogs*. They found that in this environment which is characterized by decomposition of organic litter (leaves, vegetation), ^{90}Sr , ^{137}Cs , $^{239,240}\text{Pu}$ and natural ^{210}Pb , ^{226}Ra , ^{238}U , and ^{232}Th remained mostly, and for long times in the uppermost soil layers. Schell and Colgan [281] showed that micro-organisms may influence speciation of *caesium*. Bachhuber *et al.* [282] reported on the behaviour of ^{137}Cs and ^{90}Sr in multilayered soils. They used batch experiments, column and fallout investigations, and three soils (podsol, ranker and brown soil) and concluded that column experiments, performed under conditions approaching those in nature, can be used to obtain fairly realistic information about the behaviour of these products. The influence of pH, soil type and soil organic matter con-

centration on the mobility of radio-caesium was investigated by Kerpen [283], and of *radio-caesium* and *radio-strontium* by van Bergeijk *et al.* [284]. These authors found an increased mobility of caesium by a factor of 10 when the organic matter content of the soils increased from <5% to 50%. A possible explanation of this effect could be a surface covering of clay particles by organic matter which might prevent adsorption and fixation of Cs. In contrast, the mobility of strontium decreased under similar conditions about ten times. The authors explain this tentatively with chelation and complexation of Sr^{2+} by humic and fulvic acids.

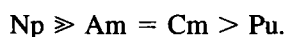
Grütter *et al.* [224, 225, 285] investigated the sorption, desorption, and exchange behaviour of *caesium*, *strontium* and *barium* in unconsolidated glaciofluvial materials from a shallow aquifer. They found a strong retardation in desorption and exchange of caesium at concentrations $>10^{-6}$ M. This effect was explained by structural changes in clay minerals (e.g., illites or chlorites, [286]) which dominate the sorption of caesium in these materials. Potassium and H^+ are the main competitors for caesium [224]. A strong association of caesium with silicates was also found by Livens and Rimmer [272]. In contrast to caesium, the sorption of strontium and barium to clay minerals is controlled by a reversible cation-exchange mechanism [225, 285].

Pimpl [287] reviewed and investigated the transfer of ^{237}Np , ^{238}Pu , ^{241}Am and ^{244}Cm from *agricultural soils* to plants. The *neptunyl* cation, $(\text{NpO}_2)^+$, is very resistant towards hydrolysis and is negligibly adsorbed by soil particles. In the presence of high carbonate concentrations Np(V) may form insoluble carbonate complexes [218]. Usually Np is very mobile in soils and is easily taken up by plants. This behaviour contrasts to other actinide elements. Based on a similar behaviour to *thorium*, Pimpl [287] assumed that *plutonium* occurred in surface soils only in the +4 oxidation state, and that it was present as very insoluble PuO_2 and $\text{Pu}(\text{OH})_4$. These species are strongly sorbed by soil surfaces. But Bidoglio [288] has demonstrated that humic acids enhanced the release of plutonium from soils. Experimental studies of the effects of organic materials on the sorption of uranium and plutonium were also reported by [289]. A thorough discussion on the effects of humic substances on binding constants, redox conditions, and kinetics of complexation of actinides, and implications on their migration in the environment was presented by Choppin [290, 291]. In a comparison of the plutonium migration at Nagasaki (residues of the atomic bomb), and in laboratory experiments, it was noticed that in-situ K_d -values were only about one-tenth of the laboratory values [292]. The authors attributed this result to differences in chemical or oxidation states of Pu, but unfortunately, they did not go further in explaining. Guillaumont and Adloff [293] discussed the behaviour of plutonium at very low environmental concentrations and questioned the validity of the mass action law at Pu concentrations of less than 100 Pu atoms.

Wildung and Garland [294] have reviewed the importance of *microbial processes* for the fate and behaviour of transuranic elements in soils, plants and animals. Bacteria, fungi and actinomycetes are capable of transporting plutonium into the cells and altering its form in cells and solution. The resulting soluble plutonium complexes exhibit mobility in soils. The forms of the complexes are not well defined. However, recently Brainard *et al.* [295] demonstrated that siderophores are extremely effective (10^3 times more effective than other chelators) in solubilizing actinides. Siderophores are low molecular weight iron chelators which are produced by microbes in response to low availability of soluble iron. Due to the abundance of siderophore-producing bacteria in soils, it is likely that the speciation of actinides may be influenced.

Aragón *et al.* [296] investigated by sequential extraction the speciation of plutonium in a soil from Palomares (Spain) which had been contaminated by debris of nuclear weapons from a plane crash. They found more than 90% of the activity of $^{239,240}\text{Pu}$ associated with sesquioxides. Unfortunately, they did not indicate the soil type and its composition. Furthermore, the different extractions showed strong and variable time dependencies which added considerably to the uncertainty of the method. Again, by extraction techniques, Livens and Baxter [297] identified major associations of plutonium with size fractions of different soils.

The information on the environmental behaviour of *americium* and *curium* is scarce. Only the +3 oxidation state is stable under normal environmental conditions. Both elements form insoluble hydroxides which are strongly sorbed by surfaces. Americium and curium are also known for the formation of stable complexes with organic ligands [230, 298–303]. Pimpl [287] gave the following decreasing sequence for soil/plant transfer:



Pimpl [287] showed that the solubility and the availability of the transuranic elements for plants was influenced by the soil type which determined the pH of the interstitial water, ion exchange and complex formation capabilities. According to Seaborg [304] the uptake by plants is hindered by hydrolysis of actinide species. Aragón *et al.* [296] found for the Palomares soil (Spain) about 60% of the Am strongly bound to the solids, whereas the remaining part was more mobile than Pu. This agrees qualitatively with the results of Pimpl. Results of Olsen *et al.* [222], obtained close to a liquid waste disposal site of the Oak Ridge National Laboratory in the USA, have demonstrated that *curium* can be extremely mobile under certain conditions, e.g., at high pH, when humic substances are released from soils and stabilize Cm in solution. Elert [305] pointed to the importance of soil parameters (i.e., mineral composition, organic matter content, pH, redox potential) for the radionuclide mobility in upper soils. They postulated that only Ra, Cs and Am

might have retention times longer than the assumed life-time of the soil. Pennders [306] noticed a remarkable similarity in the behaviour of Am and Eu on one hand (which is not surprising) and Cs and Pu on the other hand. In our opinion, the similar behaviour of the latter two elements must have different reasons: caesium is strongly bound to clay minerals, whereas the insolubility of plutonium probably results from PuO_2 or $\text{Pu}(\text{OH})_4$ (see above).

Technetium-VII is the most likely fallout form to enter surface soils. The pertechnetate ion is generally readily extractable from soils. In aerobic soils about 90% of the technetium can be assumed to remain in solution as technetate ion or to be weakly adsorbed to ion exchange sites. Less than 10% may be fixed by clays or organic complexes [273]. This contrasts to very acidic and/or anaerobic soils where only about 40% of the technetium remains mobile. Bondietti [307] found reduced species of technetium, as well as very soluble TcO_4^- in soils. Reduced technetium was associated with humic substances. The low molecular weight organic fraction was enriched in technetium. TcO_4^- did not sorb to this material. These results are in agreement with the findings of Sheppard *et al.* [308]. In a field tracer experiment [309] at an Eh of -150 mV none of the injected TcO_4^- was recovered from a hydrologically conductive fracture at a depth of 150 m. The authors concluded from this experiment that the reduction of Tc(VII) was a fast process.

The environmental behaviour of *radioiodine* has been reviewed by Liu and von Gunten [310]. Data on its chemical behaviour and speciation in surface soils are limited and still controversial. The following species were found for *inactive iodine*: I^- , IO_3^- , iodine associations with clay silicates, sesquioxides, organic matter, and possibly free iodine [311]. A similarly large variety of species has to be expected for the *radioactive isotopes of iodine*. Despite the mainly anionic nature of iodine species, a distribution coefficient (K_d) of about 6 ml g^{-1} has been proposed [312]. This would mean that only a small portion of iodine can be taken up by plants, and that radioiodine resulting from fallout would remain to a large extent in the surface soils. Norrish [313] found that soils, rich in organics and clays, retained iodine, but the sorption mechanisms were not known. Associations of iodine with organic soil components were also demonstrated by others, e.g., [314–317]. Enzymes play an important role in the iodination of humic substances [318]. The sorption of *iodine* to clays seems to occur only at $\text{pH} < 7$ [319]. At higher pH-values iodine is probably displaced by OH-groups. In general, there seems to exist a significant pH-dependency for the sorption of iodine [320] which we explain tentatively by an increase of the positive surface charges with decreasing pH (i.e., increasing H^+). Lieser and Steinkopff [321] investigated in laboratory batch experiments the sorption of *iodine* to sediments from geological formations of the planned repository for radioactive wastes at Gorleben, Germany. They found, as expected, a very small sorp-

tion of I^- onto minerals. However, the sorption to carboniferous particles was very high and irreversible, in particular, sorption to the organic compounds and the micro-organisms contained therein. Some authors, e.g., [315, 322, 323] pointed to a possible involvement of microbiology for the fixation of radioiodine to surface soils. In older publications [324, 325] a reaction of iodine with tyrosine, thiol groups and polyphenyls was proposed. Wildung *et al.* [326] noticed a significant volatilisation of iodine from soils and plants, especially during plant growth. Volatile alkyl iodides are formed in soil and plant processes (see also Chapter 3, Airborne Radionuclides).

5.3.2 Chernobyl

A vast amount of radionuclide data for soils has accumulated during and after the Chernobyl accident. However, the knowledge about their speciation is still limited and much more work is needed to arrive at a better understanding. Popov [327] investigated chemical forms of ^{90}Sr and ^{137}Cs in alluvial soils in the environment of Chernobyl by sequential extractions with water, acetic acid, HCl, and a mixture of HF and HNO_3 . His results showed that the depth distribution for both nuclides depended largely on the soil type and that they were predominantly present in a non-exchangeable form (extracted by 6 M HCl). The exchangeable fraction seemed to increase with time (1987–1991) due to the dynamics of this complicated natural system. The author concluded that the radionuclide transport was mainly due to down movement of particles, and only to a much smaller extent (25–30%) due to exchange processes. This might, in part, result from the fact that close to the damaged reactor a considerable fraction of the fallout radionuclides was incorporated into primary fuel particles [328]. This is in agreement with results of Oughton *et al.* [329] who found by sequential extractions that location-specific differences in the behaviour of ^{90}Sr and ^{137}Cs were produced mainly by the fallout speciation, and less by environmental differences. Rauret *et al.* [330] have investigated the role of organic matter for the speciation of radio-caesium in soils. For this purpose they determined caesium in five fractions: exchangeable Cs, slightly bound (extracted by pyrophosphates), moderately bound (NaOH), strongly bound (H_2O_2), residual. They noticed a smaller mobility of Chernobyl-Cs than of Cs introduced in laboratory experiments. This points again to the importance of the primary (i.e., particles) speciation. A British Steering Committee reviewed in an UK co-ordinated study the behaviour of caesium in natural systems [331]. Once in the soil, the behaviour of caesium and other radionuclides depended on the relative amounts of mineral and organic deposits. In clay rich soils caesium was strongly sorbed. In the organically rich upland soils, micro-organisms, and particularly fungi, influenced the retention of radio-caesium, especially in the important plant rooting zone. The results of this review study emphasized

clearly the need for a better understanding of the distribution between exchangeable, non-exchangeable and soil solution compartments, and the role of organic matter. Virchenko and Agapkina [332] have analysed Chernobyl radionuclides in soil solutions of a sandy-loam podzol. Only one to two percent of the radionuclides were found in this solution. Organic compounds in the solution were fractionated by gel chromatography. Strontium-90 and ^{137}Cs were associated with organic matter in the size range 10^2 – 10^4 molecular weight (MW). Strontium-90 was related to the lower MW fraction, ^{137}Cs was found among the substances of higher MW.

Several authors [333–335] observed an ageing mechanism of ^{137}Cs in soils which is manifested by a decrease in mobility and a reduced uptake by plants. In the initial fallout, ^{137}Cs was present as a cation or a simple compound. With passing time it may be fixed in the interlayers of clay minerals. Agricultural activities may also influence the uptake of caesium by plants due to physical mixing of soils and natural and synthetic additives [336].

Not much is known about the behaviour of hot particles in agricultural soils [187]. Unlike individual radionuclides which become less available to uptake by plants as time goes on, fuel fragment particles may represent a long term and increasing source of contamination due to leaching by rain and soil water. Leaching processes may be enhanced with time due to chemical attack and structural changes of the particles.

6. Conclusions

A better characterization of speciation is necessary for a thorough understanding of processes and mechanisms governing the behaviour of radionuclides in the environment. Identifying these features will require a considerable future research effort, but this is mandatory if further progress is to be made on the impact of radionuclides on the natural environment and on mankind.

More sensitive, invasive speciation methods are needed. Several very sensitive methods (mainly based on laser-induced spectroscopy) were recently introduced, but their sensitivities still need improvements. Most of today's methods are operational (e.g., sequential extractions) and give only method-dependent results, or are based on computational or experimental models which are strongly influenced by the reliability of the chosen data and assumptions. Some speciation methods furnish only information about the distribution of radionuclides among different phases or minerals, but do not characterize the chemical form of the radionuclide itself. Speciation may change during sampling and pre-concentration or in the process of the chemical analysis. Furthermore, a considerable part of the present knowledge about speciation results from comparative studies of inactive elements or isotopes at much higher concentrations than those of radio-

nuclides in the environment. Fortunately, the speciation of radionuclides follows often that of its inactive isotopes (if they exist). Despite these problems and difficulties the efforts to determine the speciation of radionuclides in the environment should be continued or possibly increased.

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