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Radionuclides in the Environment

Preface

The natural and artificial radionuclides, which are present in the upper soil, in drinking water, in food, and in the atmosphere, are the main sources of radiation exposure for living organisms. On a global average, 79 % of the radiation to which general public is exposed are from natural sources, 19 % from therapeutic application, and the remaining 2 % are from fallout of nuclear weapons testing and from use of nuclear power. 438 nuclear power plants exist in 31 countries as of June 1, 2015 with an installed electric net capacity of about 379 GW. 67 plants with planned installed capacity of 65 GW are under construction in 16 countries. More than 200 different radioactive isotopes are generated during the operation of a typical reactor, most of the them relatively short-lived and decay to low levels within a few decades. During normal operation, only a negligible fraction is set free; however, the volatile and short-lived isotopes such as I-131 can commit considerable dose to man.

Uranium is ubiquitous in nature and uranium concentrations of 1–10 mg kg^{-1} are not uncommon. By weathering of U-bearing minerals like uraninite, coffinite, pitchblende, and carnotite, uranium in its hexavalent state can be mobilized. Oxidative dissolution of minerals by the action of water releases soluble uranyl (UO_2^{2+}). Besides, U(VI) valance states III, IV, and V exist, of which IV and VI are the most common valance states at natural conditions. The oxidation of organic matter or iron in soil can reduce hexavalent uranium to the hardly soluble U(IV), which is strongly adsorbed by soil particles and forms stable complexes (hydroxides, hydrated fluorides, and phosphates) immobile in soils. In contrast, U(VI) has a high solubility. U(VI) is readily complexed by fluoride, sulfate, carbonate, as well as phosphate. U(IV) is predominant in soils with high water content at $Eh < 200$ mV, whereas U(VI) prevails in adequately aerated soils. Vertical U migration in soil is a long-term process and has two possible pathways: upward, in the case of water deficit, and downward, as a result of leaching.

Dissolved radionuclide ions can bind to solid surfaces by a number of processes often classified under sorption. The radioactive nuclides' relocation rate in soil is defined as an average velocity of downward migration after the deposition to the soil surface.

In summary, the behavior and ultimate radiological impacts of radionuclides in soils are largely controlled by their chemical form and speciation, which strongly affects their mobility, the residence time within the soil rooting zone, and availability for uptake by biota. The basic processes controlling mobility of radionuclides (and other trace elements) in soil include convective transport by flowing water, dispersion caused by spatial variations of convection velocities, diffusive movement within the fluid, and physicochemical interactions with the soil matrix.

The low concentration of radionuclides in soil makes formation of intrinsic polymeric species and formation of their pure solid phases an unlikely process. Instead, mixed phases and complexes are the dominating species. Exceptions are release of radionuclides already in particulate form such as in the case of reactor accidents or from fuel fabrication plants. However, humus and low-molecular weight are significantly involved in the mobility of radionuclides in soil. Soil redox potential, pH, the content, and composition of the organic matter and the sorption to mineral soil constituents represent the main factors controlling the chemical form of radionuclides in soil.

To achieve information on radionuclide species such as (pseudo-)colloids and particles, advanced analytical methods including nano- and micro-analytical techniques are required for the identification, isolation, and characterization of "hot" particles. Measurement of radioactivity alone is not sufficient for understanding the fundamental molecular mechanisms of environmental concern, such as migration, plant uptake, and transfer. Additional dedicated techniques such as X-ray-based high-resolution imaging or spatially resolved mass spectrometry give valuable additional information.

Transfer of radionuclides along food chains has been studied widely in the last 50 years following civilian use of nuclear energy, releases from military sites, and nuclear weapons testing on a global scale. The transfer factor (TF) for the uptake of any radionuclide from soil to plant is defined as the ratio of the dry weight concentration in plants to the dry weight concentration in a specified soil layer. The dry weight was used to reduce uncertainty, with the exception of fruits. The TF also regularly referred to as concentration ratio (CR) is the most common parameter to quantify radionuclide soil to plant transfer, when uptake by plant roots is the only process affecting transfer and wet or dry deposition on leaves is not taken into account.

The primary application of soil-to-plant transfer factors is in biosphere models used for calculating radiological consequences from routine or accidental release of radioactive substances into the environment. These models usually are designed to give conservative assessments. However, the migration and accumulation of radionuclides in the soil plant system is a complicated phenomenon, involving, e.g., leaching, capillary rise, runoff, sorption, root uptake, and resuspension into aquifer or atmosphere.

The uptake of any radioactive ion is regulated by a number of factors, i.e., physicochemical properties of the radioactive ions, the growth stage on the agricultural crop at the time of radionuclide contamination, the total amount of precipitation, the intensity of the precipitation, and the ability of the agricultural crops to hold water. The concentration of radioactive ions in agricultural crops will be different depending on the growth stage. Usually at a well-developed growth stage, the majority of deposited radionuclides will be taken up directly by areal parts of the plant.

Sometimes chelating agents and/or organic compounds also increase the radionuclide ion mobility in plant systems and reduce soil retention, which leads to an overall enhanced radionuclide uptake. Moreover, chelating agents also enhance the translocation ability within the plant itself. For remediation purposes, plants' nutrient deficiencies are beneficial because they decrease soil retention, therefore increasing plant uptake. However, the opposite, i.e., high nutrient concentration, is desirable to avoid intake into the food chain. Effectiveness depends on soil properties (especially soil pH), chemical form of the radionuclide, and the nature and concentration of chelating agent.

In any plants, radionuclides do not easily enter through the cuticular layer of the epidermis of leaves. It is rather through cracks and defects in the cuticle layer that radionuclide can enter the leaves. Alternatively, radionuclides may enter into the plant system through the stomata as well, but this pathway contributes to the total uptake only to a smaller extent. Once radionuclide entered inside the cuticle layer, specialized epidermal cells (surface veins consisting of thin-walled parenchyma tissue) are easily penetrated. Radionuclides are then actively transported inside the plant cells through the symplastic pathway (the inner side of the plasma membrane in which water can freely diffuse) and also by an exchange apparatus between phloem and xylem (vascular bundle) through the vascular rays.

Plant tolerance to radionuclides largely depends on plant competence in uptake, translocation, and sequestration of radionuclide in specialized tissues or in trichomes and cell organelles. Radionuclides which are complexed and sequestered in cellular structures become unavailable to shoots via translocation. Radionuclide binding/complexing to the cell wall is not the only plant mechanism responsible for radionuclides' immobilization into roots and subsequent inhibition of ion translocation to above ground parts. In general, vacuoles are generally considered to be the main storage site for radionuclides in plant cells and there is some evidence that phytochelatin (low-molecular binding peptides)–metal complexes are pumped into the vacuole.

The significant features of this book are related to how radionuclides are released into the environment and how the chemical speciation does influence the radionuclide migration in soil and uptake in plant system. The first four chapters deal with bioavailability of radionuclide mobility in soil. The rest of the chapters focus on radiotracers and biotransformation of radionuclides, uptake and retention of radionuclide after natural/artificial radionuclide fallout, analysis of certain radionuclide in environmental samples, methods of decreasing radionuclide transfer in the plant system from soil, and some case studies on modeling. Furthermore, the information compiled in this book will bring in-depth knowledge and enhancement in the field of radionuclide uptake and its toxicity in plants after Chernobyl and Fukushima nuclear power plants accidents.

Prof. Clemens Walther and Dr. Dharmendra K. Gupta personally thank the authors for contributing their valuable time, knowledge, and eagerness to bring this book into in this shape.

Hannover, Germany

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Sources Contributing to Radionuclides in the Environment: With Focus on Radioactive Particles

Brit Salbu, Lindis Skipperud, and Ole Christian Lind

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Abstract To assess environmental impact and risks associated with radioactive contamination of ecosystems, links must be established between the source term and deposition, ecosystem transfer, biological uptake and effects in exposed organisms. In transport, dose, impact and risk models, information on the source term and the deposition densities is therefore an essential input. Following severe nuclear events, a major fraction of refractory radionuclides can be present as radioactive particles. The particle characteristics will depend on the source and the release scenarios, and such information should be included in the source term. Furthermore, assessments are traditionally based on average bulk mass or surface activity concentrations of radionuclides in environmental compartments (Bq/kg, Bq/m^2 or

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Bq/L), assuming that a limited number of samples are representative. Localised heterogeneities such as particles will, however, be unevenly distributed, and representative sampling can be questionable. Due to structural properties, dissolution of radionuclides from particles prior to measurements may be partial. For areas affected by particle contamination, the inventories can be underestimated, and impact and risk assessments may suffer from unacceptable large uncertainties if radioactive particles are ignored. The present chapter will focus on key sources contributing to radioactivity in the environment, especially radioactive particles, and will summarise the most important particle characterisation techniques available.

Keywords Nuclear sources releasing particles • Particle characterisation techniques • Linking sources to particle characteristics

1 Release of Radioactivity in the Environment

A series of sources has contributed to radioactivity in the environment, and naturally occurring radioactive materials (NORMs) and artificially produced radionuclides are present in all ecosystems. In addition to NORM from natural processes such as the weathering of uranium (U)- or thorium (Th)-rich minerals, additional contributions originate from man-made activities associated with the front end of the nuclear weapon and fuel cycles (U mining) and from non-nuclear industries (e.g., oil and gas industries). Since 1945, a series of nuclear and radiological sources have also contributed to the release of artificially produced radionuclides into the environment, in particular sources associated with the nuclear weapon and fuel cycles.

To put the contribution of the different sources into perspective, the relative (%) contribution to the radiological consequences, expressed as the average annual radiation dose per person (mSv), can be utilised. According to the National Council on Radiation Protection and Measurement (NCRPM 2009), the average annual radiation dose per person in the USA is 6.2 mSv, while 3.0 mSv on a global scale. The contribution of different sources to the annual average person dose can be distingushed. NORM sources such as cosmic radiation and contribution from the ground including daughter nuclides like the radon and thoron gases contribute to more than 50 % of the annual dose. The exposure from man-made sources (48 %) is predominately attributed to medical diagnostics and treatments. The estimated contribution from the nuclear weapon and fuel cycle amounts to about 0.02 mSv also on the global scale. However, the natural and artificial background radiation levels are unevenly distributed and vary according to geology and altitude and especially to the distance from nuclear accidental or nuclear test sites.

To put the contribution of different sources included in the nuclear weapon and fuel cycles into perspective, UNSCEAR (2000) has estimated their contribution to

Table 1 Collective effective dose to the public from radionuclides released from the nuclear weapon and fuel cycles (UNSCEAR 2000)

Source	Normalised collective effective dose (manSv/GW$_e$y)
Local and regional effects	1995–1997
Mining	0.19
Milling	0.008
Mine and mill tailings (releases over 5 years)	0.04
Fuel fabrication	0.003
Reactor operation	
Atmospheric	0.4
Aquatic	0.04
Reprocessing	
Atmospheric	0.04
Aquatic	0.09
Transportation	<0.1
Total (rounded)	0.91
Solid waste disposal and global effects	
Mine and mill tailings	
Releases of radon over 10000 y	7.5
Reactor operation	
Low-level waste disposal	0.00005
Intermediate-level waste disposal	0.5
Reprocessing solid waste disposal	0.05
Globally dispersed radionuclides (truncated to 10000 years)	40
Total (rounded)	50

the collective effective dose to members of the public, normalised according to energy produced per year (mSv/GW$_e$y). As demonstrated in Table 1, the major contributors to environmental contaminations are the global dispersion (atmospheric nuclear weapons tests, release from nuclear accidents) and mining. In contrast to NORM which includes naturally occurring isotopes of a limited number of stable elements, a series of radionuclides is produced in weapon tests and in reactors. Fission products, activation products and transuranics are signatures of the weapon and fuel cycle, while the contribution of the "NORM" nuclides ^{3}H and ^{14}C also is substantial.

To assess environmental impact and risks associated with radioactive contamination of ecosystems, links must be established between the source term and deposition, ecosystem transfer, biological uptake and effects in exposed organisms. In transport, dose, impact and risk models, information on the source term and the deposition densities is needed as input. The source term is usually a qualitative and quantitative description of radionuclides released from a source, used as input to models describing the air or water transport, dispersion and deposition of radionuclides in affected ecosystems. The source term is most often estimated from the source inventory (% released) and provides information on the amount of radionuclides released (Bq), the time development of the release, plume height and energy content of the release. In most air dispersion models, the source term input as Bq is assumed to represent aerosol transport (e.g. similar to sulphate aerosols adapted from acid rain research), while in most marine transport models, Bq refers to simple chemical species behaving conservatively. When refractory radionuclides such as uranium (U) and plutonium (Pu) are released during nuclear events, however, a major fraction is associated with particles, ranging from submicrons to fragments.

Radiological assessments are also most often based on average bulk mass or surface activity concentrations of radionuclides in water (Bq L^{-1}), soils, sediments (Bq kg^{-1} or Bq/m^2) or biota (Bq kg^{-1}), assuming that radionuclides are homogeneously distributed as simple chemical species and that a limited number of samples are representative of the deposition. It is generally not recognised that releases can include radioactive particles that often contain a significant fraction of the bulk sample activity present in the environment (IAEA 2011). Furthermore, localised heterogeneities such as particles will be unevenly distributed and the assumption of representative sampling can be questionable. Due to structural properties, dissolution of radionuclides from particles prior to measurements may also be partial (Oughton et al. 1993). Furthermore, the inherent differences in transport, mobility and bioavailability of particle-bound radionuclides compared with radionuclide species such as molecules, ions or complexes have largely been ignored in radiochemistry, radioecology and radiation dosimetry. For areas affected by particle contamination, the inventories can be underestimated, and the assessment of impact and risk to human health and the long-term ecological consequences can suffer from unacceptable large uncertainties if radioactive particles are ignored (Salbu 2009; Salbu et al. 2004).

Radionuclides released from a source and deposited in different ecosystems can be present in different physico-chemical forms, such as low molecular mass (LMM) species, colloids or nanoparticles as well as pseudocolloids, particles and fragments (Salbu 2000a, b). LMM species are believed to be mobile and potentially bioavailable, colloids are mobile, while particles can be retained in sinks such as soils and sediments. Due to remobilization processes, however, contaminated soils and sediments can act as diffuse sources of radionuclides in the future. Thus, information of radionuclide species released from a source and deposited in the environment as well as transformation of radionuclide species over time is essential for assessing ecosystem transfer and uptake in exposed organisms (Fig. 1).

Radioactive particles are defined as a localised aggregation of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background (IAEA 2011). In water, particles are defined as entities having diameters larger than 0.45 μm, i.e. entities that will settle due to gravity. Radionuclide species within the size range 0.001–0.45 μm are referred to as radioactive colloids or pseudocolloids, while species less than 1 nm (10^3 Da) is referred to as low molecular mass (LMM) species. For soils and sediments, grain-size analysis differentiates between categories of sand (0.062–2 mm), silt (4–62.5 μm) and clays (1–4 μm), and particles larger than 2 mm should

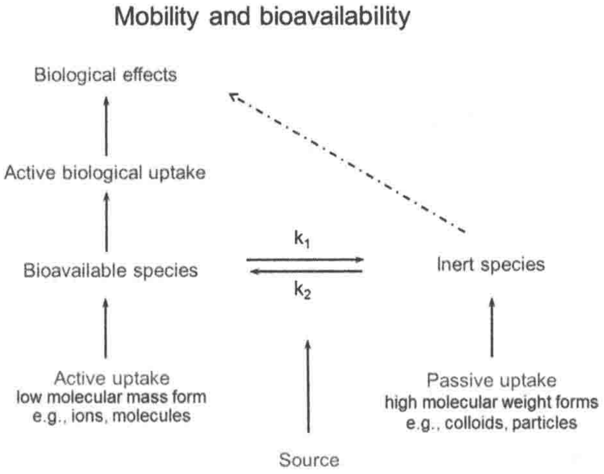

Fig. 1 Radionuclides released from a source can be present in different physico-chemical forms. LMM species are believed to be potentially bioavailable, while particles can be retained in, for instance, filtering organisms. The system is dynamic; due to transformation processes, the fraction of LMM species can decrease due to interactions with soil compartment; due to particle weathering, LLM species can be produced over time. The distribution of radionuclide species and kinetics are essential for assessing uptake, effects, impact and risks (Salbu 2000b)

be referred to as fragments. In air, radioactive particles ranging from submicrons in aerosols to fragments are classified according to the aerodynamic diameters, where particles less than 10 μm are considered respiratory. These categories are operationally based, and there are gradual transitions between categories. Due to interactions and transformation processes in the environment, particle growth mechanisms and dispersion processes will alter the original distribution of radionuclide species deposited in an ecosystem. The presence of radioactive species ranging from micrometre-sized particles to fragments can be identified by imaging techniques such as digital autoradiography (Salbu 2000b), reflecting their inhomogeneous distributions in water, sediments and soils. To obtain information on radionuclide species including particle characteristics, more advanced analytical techniques are needed (Sect. 2).

Following historical nuclear events, refractory radionuclides such as U and Pu were to a certain extent associated with particles, ranging from submicrons to fragments, containing fission products, activation products and transuranics (Sect. 3). Severe nuclear events include nuclear weapon tests and nuclear reactor explosions or fires. Conventional detonation of nuclear weapons, safety trials and the use of depleted uranium ammunition include the release of matrix particles, often ranging from submicron to fragments. Reprocessing facilities and civil reactors are also sources of radioactive colloids and particles via authorised or accidental releases. Furthermore, radioactive particles are identified in sediments in the close vicinity of radioactive waste dumped at sea. In addition, radioactive particles containing U, Th or progenies are identified at NORM sites such as U mining sites or associated with scale from the oil and gas industry. Thus, whenever refractory radionuclides are released following nuclear events, radioactive particles should also be expected.

Radioactive particles are formed due to critical (explosions, fires) or subcritical (corrosion processes) destruction of fuel, weapon matrices and other nuclear or radiological materials. During nuclear events under high-temperature and high-pressure conditions such as nuclear weapon tests (e.g., Semipalatinsk, Kazakhstan; Marshall Islands), the particle formation depends on the weapon materials and other major components such as metals (iron) in the fireball, as well as the yield and altitude of the blast. During the blast, fission and activation products as well as transuranics are formed. When the fireball temperature decreases, condensation processes take place as well as decay processes of the produced radionuclides. Due to differences in volatility, chemical properties and half-lives, the particle composition will depend on fractionation of produced radionuclides, and daughter nuclides can be depleted in particles. Thus, isotope or atom ratios of transuranic elements can be used for source identification. The particle size distribution, morphology and structure are also dependent on the type of explosion. Near-surface detonations produce large glassy soil containing often highly radioactive particles. Bursts at high altitudes in the atmosphere will produce small spherical particles which can remain suspended for considerable periods of time. Following conventional detonation of nuclear weapon (e.g., Thule, Greenland; Palomares, Spain) or the use of depleted uranium ammunition, particles are made from the mechanical destruction of weapon materials and the containment. Similarly, at high-temperature and high-pressure release scenarios (reactor explosion, fire), solid materials can liquefy, volatiles will escape, while refractory transuranics and fission and activation products can remain when droplets are solidified. Furthermore, interactions with construction materials such as moderator and zircaloy in reactors are essential for the products formed, i.e. the formation of metal–metal crystalline structures such as U–Zr or U–carbide compounds as observed after the Chernobyl accident (Salbu et al. unpublished). In contrast to hydrogen explosions, the presence of air during a fire will influence on the structure and oxidation states of released radionuclides. Thus, the composition of particles released in a nuclear reactor accident will reflect the characteristics of refractory elements in the source (burn-up) and its containment, while the release scenario (temperature, pressure and presence of oxygen) will influence the particle size distribution, crystallographic structures and oxidation states (Sect. 3) of relevance for ecosystem transfer.

Releases under low-temperature conditions are most often associated with corrosion processes damaging the source containment and allowing releases to occur. The extent of corrosion depends on physical conditions of containments as well as on the surroundings (e.g., water pH, redox, temperature). Due to corrosion of depleted uranium (DU) ammunition penetrators buried in sand, oxidised DU particles were released (Lind et al. 2009; Salbu et al. 2005). Due to corrosion, leakages of waste from containers dumped in the fjords of Novaya Zemlya are significant (Salbu et al. 1997). Due to corrosion of U–Al fuel misplaced in air ducts at the Windscale Pile, about 20 kg of U as U–Al particles were released through the air-cooled ducts (Salbu 2000a). Particles and colloids have also been released from nuclear installations as authorised discharges via pipelines to the sea (Sellafield and La Hague reprocessing facilities) (Salbu et al. 1993, 2003). Such particles can reflect the composition of the waste streams as well as represent reminiscences of the industrial processes (residues from exchange resins). The characteristics of particles obtained under low-temperature conditions will be distinctly different from those released under high-temperature–pressure conditions (Sect. 3).

The source and release scenarios, including physical characteristics such as temperature, pressure and redox conditions, are important determinants of the physico-chemical forms of released and deposited radionuclides and thereby their mobility, biological uptake and effects of consequences for affected ecosystems. To obtain information on particle characteristics, advanced techniques and equipment are needed (Sect. 2). Using such techniques, information on particle characteristics associated with different nuclear and radiological sources and different release scenarios can be obtained (Sect. 3).

2 Particle Characterisation Techniques

Key particle characteristics influencing mobility and ecosystem transfer, biological uptake and effects include particle size distributions, surface and bulk (3D) elemental composition, morphology, structure, density and oxidation state influencing the particle weathering rates (Salbu 2001). Due to their small sizes, often in the range of submicron to micrometres, radioactive particles can be difficult to locate, identify and characterise. It is likely that the lack of a reliable procedure for particle identification often leads to negligence of radioactive particles and thereby underestimation of the role they play in environmental contamination. When located, isolated and extracted, several solid-state speciation techniques can be utilised to characterise particles identified in the environment. In addition, atom or isotopic ratios can be utilised for source identification purposes.

A number of analytical tools have been applied in radioactive particle research (Table 2) as also discussed in IAEA (2011). For radionuclides in waters, filtration (<0.45 μm) and ultrafiltration (nm to μm range membranes) combined with radioanalytical techniques may be applied to distinguish ionic species and colloidal and particulate material (Salbu 2000b). To separate particles from air and provide estimates on the size distribution, cascade impactors with membranes having different cut-off levels (μm to mm) are frequently used in combination with radioanalytical methods. In contaminated areas, hot spots can be identified using portable detectors. In the laboratory, radioactive heterogeneities may be identified using imaging techniques, repeated sample mixing (Bunzl 1998; Bunzl and Tschiersch 2001) or splitting (Bunzl 1997) combined with gamma spectrometry. For contaminated soils and sediments, biological material and filters from air or water fractionation procedures, imaging techniques such as digital phosphor