Clemens Walther · Dharmendra K. Gupta Editors

Radionuclides in the Environment

Influence of chemical speciation and plant uptake on radionuclide migration



Radionuclides in the Environment

Clemens Walther • Dharmendra K. Gupta Editors

Radionuclides in the Environment

Influence of chemical speciation and plant uptake on radionuclide migration



Editors Clemens Walther Gottfried Wilhelm Leibniz Universität Hannover Institut für Radioökologie und Strahlenschutz (IRS) Hannover Germany

Dharmendra K. Gupta Gottfried Wilhelm Leibniz Universität Hannover Institut für Radioökologie und Strahlenschutz (IRS) Hannover Germany

ISBN 978-3-319-22170-0 ISBN 978-3-319-22171-7 (eBook) DOI 10.1007/978-3-319-22171-7

Library of Congress Control Number: 2015955144

Springer Cham Heidelberg New York Dordrecht London © Springer International Publishing Switzerland 2015

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media (www.springer.com)

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

Clemens Walther Dharmendra K. Gupta

Contents

Sources Contributing to Radionuclides in the Environment: With Focus	
on Radioactive Particles Brit Salbu, Lindis Skipperud, and Ole Christian Lind	1
Mobility and Bioavailability of Radionuclides in Soils	37
The Influence of Edaphic Factors on Spatial and Vertical Distributionof Radionuclides in SoilSnežana Dragović, Jelena Petrović, Ranko Dragović, Milan Đorđević,Mrđan Đokić, and Boško Gajić	61
Modelling Speciation and Distribution of Radionuclides in AgriculturalSoilsVolker Hormann	81
Radiotracers as a Tool to Elucidate Trace Element Behaviour in the Water–Sediment Interface	101
Uptake and Retention of Simulated Fallout of Radiocaesium and Radiostrontium by Different Agriculture Crops	115
Root Uptake/Foliar Uptake in a Natural Ecosystem	133
Assessment of Radioactivity in Forest and Grassland Ecosystems P.K. Manigandan, B. Chandar Shekar, and D. Khanna	147
Terrestrial Environmental Dynamics of Radioactive Nuclides	159

Biotransformation of Radionuclides: Trends and Challenges		
Methods for Decrease of Radionuclides Transfer from Soil to Agricultural Vegetation	185	
Bacterial Diversity in Clay and Actinide Interactions with Bacterial Isolates in Relation to Nuclear Waste Disposal	209	
Analysis of Radionuclides in Environmental Samples	231	
Uncertainty Analysis and Risk Assessment	255	

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

Brit Salbu, Lindis Skipperud, and Ole Christian Lind

Contents

1	Release of Radioactivity in the Environment		
2	Particle Characterisation Techniques		
	2.1	Identification and Isolation of Radioactive Particles	10
	2.2	Nano- and Microfocusing Analytical Techniques	10
	2.3	Identification of Isotope Ratios for Source Identification of Single Particles Using	
		MS Techniques	13
3	Link	ing Sources and Particle Characteristics	15
	3.1	Particles Originating from Testing of Nuclear Weapons	16
	3.2	Particles Released During Nuclear Accidents	19
	3.3	Particles Originating from Nuclear Reprocessing Activities	21
	3.4	Particles Associated with Dumping of Waste	24
	3.5	Nuclear Accidents Involving Satellites	25
	3.6	Conventional Detonation of Nuclear Weapons	25
	3.7	Depleted Uranium Ammunitions	27
	3.8	Radioactive Particles of Naturally Occurring Radioactive Material Origin	28
4	Cone	clusion	28
Re	ferend	ces	30

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 term. Furthermore, assessments are traditionally based on average bulk mass or surface activity concentrations of radionuclides in environmental compartments (Bq/kg, Bq/m² or

CERAD, Department of Environmental Sciences, Norwegian University of Life Sciences, 1432 Aas, Norway e-mail: brit.salbu@nmbu.no

B. Salbu (🖂) • L. Skipperud • O.C. Lind

[©] Springer International Publishing Switzerland 2015

C. Walther, D.K. Gupta (eds.), *Radionuclides in the Environment*, DOI 10.1007/978-3-319-22171-7_1

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

	Normalised collective effective dose			
Source	(manSv/GW _e v)			
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			

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

the collective effective dose to members of the public, normalised according to energy produced per year (mSv/GW_ey). 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 ³H and ¹⁴C 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 μ m, i.e. entities that will settle due to gravity. Radionuclide species within the size range 0.001–0.45 μ m are referred to as radioactive colloids or pseudocolloids, while species less than 1 nm (10³ 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 μ m) and clays (1–4 μ m), and particles larger than 2 mm should