Dharmendra Kumar Gupta
Clemens Walther *Editors*

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Preface

Atomic nuclei which are not stable but decay by emission of highly energetic radiation are called radionuclides. They are omnipresent in nature, some of them with half-lives exceeding the age of the solar system. Amongst these are, e.g., potassium-40, uranium-238, uranium-235, and thorium-232. Uranium is found in many types of soil and rocks (concentrations ranging from 0.003 ppm in meteorites to 120 ppm in phosphate rock). In addition, there are shorter lived radionuclides produced by natural processes such as interaction of cosmic radiation with the earth's atmosphere. Carbon-14, beryllium-10, and tritium are examples. Human activities such as nuclear weapon's testing in the 1960s, accidents involving nuclear material (military and peaceful use of nuclear power), lost and orphan sources from, e.g. medical use add to the radioactive inventory. Further sources are mining activities. Any matter originating from deep underground may contain considerable amounts of natural radioactive matter (NORM). For instance, the production of oil, gas, or phosphate fertilizers goes hand in hand with the release of considerable amounts of uranium and decay products. Enhanced radiation levels from tailing of these uses are called TENORM (technically enhanced NORM). Also, regenerative energies are not free from radiation risks. Geothermal water used for energy production may contain high levels of radium from the uranium and thorium decay series' accumulating in filters and scales.

Once radionuclides are deposited on the soil surface, they eventually are incorporated into the soil structure, taken up by plants and, via the food chain, enter animals, and also humans. A 75 kg human contains approximately 9,000 Bq of natural radioactivity in his body, mainly due to K-40 and C-14. Some organs such as the thyroid gland and also certain plants may enrich radionuclides, as is known for seaweed, enriching iodine by a factor >10.000 L Kg^{-1}. During the course of evolution cells learned to repair damages caused by the ionizing radiation emitted from radioactive decay (alpha, beta or gamma radiation) and the damages caused by secondary species generated from ionizing radiation such as free oxygen radicals (ROS). As a rule of thumb organisms are the more sensitive to radiation the higher their DNA content is. However, at too high radiation levels even simple organisms and cells will suffer and finally the total organism will be damaged or die. While damage from the ionizing radiation to the cells DNA is most important at high dose the chemical toxicity of many radioactive isotopes plays an important role. Uranium, thorium, plutonium, and lead, to name just a few, are heavy metals. In these cases, stress to cells due to chemical toxicity adds to effects of ionizing radiation.

Like heavy metals, radionuclides cannot be naturally or synthetically degraded. Therefore, radionuclides become a risk factor to public health when exposed and/or deposited in soil and water.

Being sessile in nature, plants are exposed to radionuclides which are released and disseminated into the environment as dry or wet deposition on soil or water. Both routine and accidental incorporation of nuclear wastes in the environment cause radionuclides swallowing, where soil to plant transfer of such materials take place. However, uptake of the radionuclides by plants depends upon several factors including mode of interaction with the materials and physiological characteristics of the species and factors like concentrations, bioavailability, and mobility of radionuclides in surface and subsurface geologic systems. The concentration, mobility, and bioavailability of radionuclides depend upon the quality, quantity, and the rate of release of radionuclides present at the source; different hydrological factors, such as dispersion, advection, and dilution; and geochemical processes, like complexation at aqueous phase, pH, solid/liquid distribution coefficient, reduction/oxidation (redox), adsorption/desorption and ion exchange, precipitation/dissolution, diffusion, colloid-facilitated transport, exchangeable potassium ion distribution, anion exclusion and organic matter contents. Absorption and distribution of the contamination in plants may take place either through direct (exposures at aerial organs) or indirect (through root systems in soil related contamination) routes, which varies considerably in different plant species especially in case of long-lived radionuclides. Furthermore, biological activity or physical changes in the soil properties/texture (like drying and subsequent cracking of soils) and colloid-facilitated transport may augment the mobility and/or affectivity of certain radionuclides Plant tolerance to metals depends largely on plant efficiency in uptake, translocation, and further sequestration of metals in specialized tissues or in trichomes and cell organelles. Metals which are complexed and sequestered in cellular structures become unavailable for translocation to the shoot. Metal binding to the cell wall is not the only plant mechanism responsible for metal immobilization into roots and subsequent inhibition of ion translocation to the shoot. The vacuole is generally considered to be the main storage site for metals in yeast and plant cells and there is evidence that phytochelatin—metal complexes are pumped into the vacuole in plants.

Though radionuclide uptake into plants and consequently into the food chain is generally undesired. A very effective and even selective uptake of certain elements by plants can, however, be even helpful in remediating contaminated soils. This concept is known as phytoremediation. Phytoremediation of radionuclides has many advantages over the traditional treatments. Firstly, in phytoremediation the soil is treated in situ, which does not cause further disruption to the soil dynamics. Secondly, once plants are established, they remain for consecutive harvests to continually remove the contaminants. Lastly but not least, phytoremediation reduces the time workers are exposed to the radionuclides. Finally, phytoremediation can be used as a long term treatment that can provide an affordable way to restore radionuclide contaminated areas. For phytoremediation of radionuclides to be successful, a few criteria have to be met. The most important is that the radionuclides be spread throughout a huge area and be present in very low-level concentrations. The radionuclides must be bioavailable in water/soil solution for plants to up take them into roots. The plants themselves must also be tolerant of the radionuclides when they are accumulated into their biomass. The best plants for phytoremediation are those that have an extensive root system and adequate above-ground biomass.

When plants are exposed to ionizing radiation, molecular and cellular effects are induced directly through energy transfers to macromolecules or indirectly through a water radiolytic reaction producing reactive oxygen species (ROS). By energy transfer from the radiation field to plant tissue, ionizing radiation can directly induce DNA strand breaks, lipid oxidation, or enzyme denaturation. Besides directly damaging macromolecules, potentially toxic ROS can be generated during radiolysis of water, indirectly inducing cellular damage. As ROS are also produced under natural metabolism and also function as signalling molecules regulating normal growth, development, and stress responses, plants also possess an antioxidative defense system comprising enzymes (e.g., superoxide dismutase (SOD) and catalase (CAT)) and metabolites (e.g., ascorbate and glutathione) to regulate the amount of ROS in cells. Plant tolerance mechanisms require the coordination of complex physiological and biochemical processes, including changes in global gene expression. Plants employ various strategies to cope with the toxic effects of radionuclides like metals or metalloids.

Resistance to radionuclides stress can be achieved by “avoidance” when plants are able to restrict metal uptake, or by “tolerance” when plants survive in the presence of high internal metal concentration. Avoidance involves reducing the concentration of metal entering the cell by extracellular precipitation, biosorption to cell walls, reduced uptake, or increased efflux. In a second type of situation, radionuclides are intracellularly chelated through the synthesis of amino acids, organic acids, glutathione (GSH), or metal-binding ligands such as metallothioneins (MTs), phytochelatins (PCs), compartmentation within vacuoles, and upregulation of the antioxidant defense and glyoxalase systems to counter the deleterious effects caused by ROS.

It is an intriguing question whether the toxicity effect induced by heavy metals was the result (at least partially) of signalling pathways evolving the action of the formed substances, or parallel direct metal action and signalling pathways. The molecular mechanisms of signal transduction pathways in higher plant cells are essential to vital processes such as hormone and light perception, growth, development, stress resistance, and nutrient uptake from soil and water. Heavy metals interfere with cell signalling pathways. In fact, it might be hypothesized that metals-induced deregulation of signaling events significantly participates in the metal toxicity response, as well as in damage development.

The main purpose of the present book is to focus on the mechanistic (microscopic) understanding of radionuclide uptake by plants from contaminated soils, both, in order to understand the risks originating from plant uptake and the benefits by potential use for phytoremediation.

The key features of the book are related to the radionuclide toxicity in plants and how the radioactive materials are taken up by plants and cope up from their toxic responses. Some chapters deal with how soil classification affects the radionuclide uptake in plants. Other chapters focus on natural plant selection, speciation of actinides, kinetic modeling, and some case studies on cesium and strontium after radiation accident. Overall, the information compiled in this book will bring in-depth knowledge and advancement in the field of radionuclide toxicity and their remediation through plants in recent years.

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

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Contents

Phytoremediation of Radionuclides: A Report on the State of the Art

Bhagawatilal Jagetiya, Anubha Sharma, Akash Soni and Umesh Kumar Khatik

Abstract Radionuclides mobilization through extraction from ores and processing for various applications has led to the discharge of these harmful elements into the environment. These contaminants pose a great risk to human health and environment. Remediation of radionuclides and toxic heavy metals deserves the proper attention. Conventional remediation methods used for polluted environments have many limitations including high costs, alteration in soil properties, and disruption in soil native microflora. Alternatively, phytoremediation can serve as a prospective method for decontamination and rehabilitation of polluted sites. The term phytoremediation actually refers to a diverse collection of plant-based technologies, i.e. either naturally occurring or genetically engineered plants are used for cleaning the contaminated environment. Phytoremediation techniques are eco-friendly, cost-effective, easy to implement, and offer an aesthetic value and solar-driven processes with better public acceptance. Practicing various agronomic alterations as well as spatial and successful combination of different plant species assures maximal phytoremediation efficiency. Plants and microorganisms can be genetically modified to remediate the contaminated ecosystems at an accelerated rate. We can harvest better results from phytoremediation technologies by learning more about the different biological processes involved. The future of phytoremediation comprises of ongoing research work and has to go through a developmental phase and several technical barriers. Several attempts still need to be performed with multidisciplinary approach for successful future phytoremedial programmes. This report comprehensively reviews the background, techniques, concept and future course in phytoremediation of heavy metals, particularly radionuclides.

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Contents

1 Introduction

Scientific and technological progress has occurred with human evolution. New challenges have arisen due to global development, especially in the field of environmental protection and conservation (Bennett et al. 2003). The mobilization of radionuclides through mining, accidents, spills, explosions, weapon fabrication, testing (Madruga et al. 2014), dumping of wastes (Richter 2013) and radioisotopes used in medicines (Frédéric and Yves 2014) has led to the discharge of these elements into the ecosystem. The problem of heavy metal including radionuclide pollution is becoming more and more serious with increasing anthropogenic activities such as industrialization and disturbances of natural biogeochemical cycles (Černe et al. 2010; Fulekar et al. 2010; Wuana and Okieimen 2011; Ali et al. 2013).

^{238}U, ^{232}Th and ^{40}K are three long-lived naturally occurring radionuclides present in the earth crust. Generally, two sources of environmental radionuclides are natural (mainly from the ^{238}U, ^{232}Th series) and artificial (Tawalbeh et al. 2013). U, Th, Cs, Co and Ce are the most common ions found in low-level liquid radioactive wastes (Hafez and Ramadan 2002). A set of radionuclides, including ^{3}H, ^{14}C, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, ^{237}Np, ^{241}Am, as well as several U and Pu isotopes, from the nuclear-related activities, are of special environmental importance due to their abundance, mobility or toxicity (Hu et al. 2010). Metal mining activities and phosphate fertilizer factories produced the waste enriched in radionuclides from the U series including ^{230}Th, ^{226}Ra and ^{210}Pb (SanMiguel et al. 2004). Radioactive isotopes such as ^{14}C, ^{18}O, ^{32}P, ^{35}S, ^{64}Cu and ^{59}Fe are widely used as tracers in plant physiology and biochemistry (Dushenkov et al. 1999). Contamination of soils with typical fission product radionuclides, such as ^{137}Cs and ^{90}Sr, has persisted for far longer (Zhu and Shaw 2000). Nuclear facilities, repository of nuclear waste, tracer and application in the environmental and biological researches release the radionuclides including ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{59,63}Ni, ^{89,90}Sr, ^{99}Tc, ^{129}I, ^{135,137}Cs, ^{210}Pb, ^{226,228}Ra, ^{237}Np, ^{241}Am and isotopes of Th, U and Pu (Hou and Roos 2008). Medical radioisotopes cover a wide variety of radionuclides—from short-lived pure gamma emitters such as ^{99m}Tc and ^{123}I for diagnostic purposes to longer-lived therapeutic isotopes such as ^{131}I, ^{7}Be, ^{67}Ga, ^{153}Sm and ^{197}Hg (Fischer et al. 2009). It has been estimated that, on average, 79 % of the radiation to which humans are exposed is from natural sources, 19 % from medical application and the remaining 2 % from fallout of weapons testing and the nuclear power industry (Wild 1993).

However, most of the public concern from radionuclides has been due to the global fallout from nuclear weapons testing and the operation of nuclear facilities. Both of these activities have added a substantial amount of radionuclides into the environment and have caused radionuclide contamination worldwide. Radionuclides in soils are taken up by plants and are available for further redistribution within food chains. Radionuclides in the environment can, therefore, eventually be passed through food chains to human beings and represent an environmental threat to the health of human populations (Zhu and Shaw 2000). The migration of radionuclides in the environment depends on many factors, such as physicochemical, biological, geochemical and microbial influences, soil and water properties, air, flora and specific interactions of radionuclides with vegetation or other organisms where they accumulate (Nollet and Pöschl 2007; Cerne et al. 2010). Radionuclides which have been responsible for major environmental concern are listed in Table 1.

Elevated metal concentrations in the environment also have wide-ranging impacts on animals and plants. For instance, human exposure to a variety of metals causes wide range of medical problems such as heart disease, liver damage, cancer, neurological problems and central nervous system disorders (Roane et al. 1996). Radionuclides can enter human body through ingestion, inhalation and external irradiation. The ingested radionuclides could be concentrated in various parts of the body. ^{238}U accumulates in lungs and kidneys, ^{232}Th in lungs, liver and skeleton tissues and ^{40}K in muscles (Samat and Evans 2011). Depositions of large quantities of these radionuclides in organs affect the health conditions such as

Table 1 Sources of radionuclides in the environment

Radionuclide	Sources	Reference
Uranium ($^{235,\ 238}$U)	Natural, mining, milling, nuclear waste disposal	Chabalala and Chirwa (2010)
Thorium (^{232}Th)	Natural, mining, milling and processing, phosphate fertilizer production, tin processing, industrial boilers, military operations	Atwood (2010), Tawalbeh et al. (2013)
Radium ($^{226,\ 228}$Ra)	Uranium decay product from mill tailing	Madruga et al. (2001), Cerne et al. (2010)
Cobalt (^{60}Co)	Car, truck and airplane exhausts, burning coal and oil, industrial processes, nuclear medicines	Simeonov and Sargsyan (2008)
Iodine (^{131}I)	Nuclear test (underground), fuel reprocessing, spent nuclear fuel	Hu et al. (2010)
Strontium (^{90}Sr)	Spent nuclear fuel, nuclear accidents, nuclear fallout, nuclear fission, nuclear power plants, radioactive tracer in medical and agricultural studies	Hu et al. (2010), ATSDR (2004)
Caesium (^{137}Cs)	Nuclear power stations	Stohl et al. (2012)
Carbon (^{14}C)	Natural and nuclear reactor	Zhu and Shaw (2000)
Potassium (^{40}K)	Natural	Zhu and Shaw (2000)
Plutonium (^{239}Pu)	Nuclear reactor	Zhu and Shaw (2000)

weakening the immune system induces various types of diseases and the increase in mortality rate. Metal toxicity in plants can cause stunted growth, leaf scorch, nutrient deficiency and increased vulnerability to insect attack (Roane et al. 1996). The carcinogenic nature and long half-lives of many radionuclides make them a potential threat to human health. Plant uptake of radionuclides into the human food chain is one of many vectors used for calculating exposure rates and performing risk assessment (Rosén et al. 1995). Geras'kin et al. (2007) performed long-term radioecological investigations and concluded that adverse somatic and genetic effects are possible in plants and animals due to radium and uranium–radium contamination in the environment.

The removal of radioisotopes from soil is theoretically simple to achieve. Soil is moved offsite for leaching/chelating treatments and then returned to its previous location. However, in practice, the movement of large quantities of soil for decontamination is environmentally destructive and costly due to transportation. It also increases the risk of releasing potentially harmful radionuclides into the atmosphere as particulate matter (Entry et al. 1996). Safe and cost-effective methods are needed for removing radionuclides and heavy metals from the contaminated soils (Phillips et al. 1995). All the conventional remediation methods used for radionuclide-polluted environments have serious limitations. Over the past decade, there has been increasing interest for the development of plant-based remediation technologies, which have the potential to be environmentally sound, a concept called phytoremediation (Laroche et al. 2005; Jagetiya and Purohit 2006; Jagetiya and Sharma 2009; Roongtanakiat et al. 2010; Borghei et al. 2011; Jagetiya et al. 2011). The concept of phytoremediation was suggested by Chaney (1983). It is an aesthetically pleasing mechanism that can reduce remedial costs, restore habitats and clean up contamination in place rather than entombing it in place or transporting the problem to another site (Bulak et al. 2014; Kamran et al. 2014). Phytoremediation can cost as less than as 5 % of alternative clean-up methods (Prasad 2003). The thriving plants display efficiency for remediation; they act as natural vacuum cleaners sucking pollutants out of the soil and depositing them in various plant parts (Rajalakshmi et al. 2011).

2 Sources of Radionuclides in the Environment

Radionuclides make their way in the environment from natural and anthropogenic sources. The most common natural sources are weathering of minerals, erosion and volcanic eruptions, while anthropogenic sources include nuclear weapons production and reprocessing, nuclear weapons' testing, uranium mining and milling, commercial fuel reprocessing, geological repository of high-level nuclear wastes and nuclear accidents. The other potential sources are coal combustion, cement production, phosphate fertilizers production and its use in agriculture management (Nollet and Pöschl 2007).

Nuclear weapons production and reprocessing programs produce high-level waste liquid and sludge. Fissile isotopes such as ^{235}U, ^{239}Pu and ^{238}U are used together with the radionuclide ^{3}H and are separated from fission products in spent nuclear reactor fuels to produce weapons-grade fuel (Hu et al. 2010).

Nuclear weapons testing has released considerable amount of radionuclides in the environment. Choppin (2003) reported that over 2×10^{8} TBq of radioactivity has been released into the atmosphere from worldwide nuclear weapons' tests. In terms of radioactivity, ^{3}H, ^{90}Sr, ^{137}Cs, ^{241}Am and Pu isotopes are currently the radionuclides of great importance. Long-lived ^{14}C, ^{36}Cl, ^{99}Tc, ^{129}I, ^{237}Np, as well as several U and Pu, isotopes are important.

Nuclear power plants produce 200 radionuclides during the operation of a typical nuclear reactor in which radionuclides decay to low levels within a few decades (Crowley 1997). A number of radionuclides are emitted from normal operation of nuclear reactor. Based on combined worldwide operable nuclear reactors of 3.72×10^{5} MWe (World Nuclear Association 2007), the annual discharge of ^{14}C worldwide is about 60 TBq Y^{-1}.

The U mining and the milling processes of raw material containing uranium and thorium are one of the main causes of discharging of radionuclides into the environment, mainly from the tailings. The radionuclides in uranium mill tailings includes ^{238}U, ^{235}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{222}Rn. ^{238}U and ^{230}Th are long-lived α-emitters, whereas ^{222}Rn is an inert radioactive gas with a short half-life, which has been identified as an important carcinogen. In addition to radioactivity, uranium mill tailings are associated with elevated concentrations of highly toxic heavy metals. Oxidation of high-sulphide content in uranium tailings generates acidic waters and increases the release of radioactive and hazardous elements (Abdelouas 2006).

Commercial fuel reprocessing results into the discharge of ^{99}Tc and ^{129}I (liquid and gaseous) into the sea and atmosphere from the nuclear fuel reprocessing plants (Hu et al. 2010). In addition to environmental contamination, a principal concern with fuel reprocessing has always been the possibility of the diversion of fissile material, mainly ^{235}U and ^{239}Pu, for weapons production. However, other fissile nuclides, such as ^{237}Np and Am, may be separated during reprocessing (Ewing 2004).

Geological repository of high-level nuclear wastes Nuclear energy production and research facilities create waste in the form of spent nuclear fuel. Spent nuclear fuel remains highly radioactive for thousands of years. Separating this waste from people and the environment has been a challenging issue for all countries with nuclear power (Hu et al. 2010). High-level waste makes up around 3 % of the world's total volume, but it has approximately 95 % of the radioactivity (low- and high-level wastes combined). Countries with high-level radioactive waste and spent nuclear fuel must dispose off these materials in a geologic disposal facility called as repository (Witherspoon and Bodvarsson 2001).

Nuclear accidents It was estimated that 1.2×10^7 TBq of radioactivity was released in the Chernobyl accident (UNSCEAR 2000). Eikenberg et al. (2004) compared the total atmospheric release of long-lived fission radionuclides and actinides from the atomic bomb tests and the Chernobyl reactor explosion. In comparison with the sum of all previously performed tests, the values for ^{90}Sr, ^{137}Cs and $^{239+240}$Pu from the Chernobyl accident were in the order of 10 % and much higher for ^{238}Pu and ^{241}Am. Fallout of hot particles caused a considerable contamination of the soil surface, with ^{137}Cs up to 106 Bq m^{-2}, and 116,000 people were evacuated within a zone of 30 km distance from the reactor (Balonov 2007). Six artificial radionuclides (^{131}I, ^{134}Cs, ^{137}Cs, ^{129}mTe, ^{95}Nb and ^{136}Cs) were detected in soil samples around Fukushima Nuclear Power Plant (Taira et al. 2012). Nuclear energy sources are also utilized in some spacecraft, satellites and deep sea acoustic signal transmitters for heat or electricity generation, the two common types of nuclear energy sources are radioisotope thermoelectric generators (RTGs) and nuclear reactors. Due to the radiotoxicity and long half-life, some radionuclides are of particular concern in the radiological dispersion devices (RDD): ^{241}Am, ^{252}Cf, ^{60}Co, ^{137}Cs, ^{90}Sr, ^{192}Ir and ^{238}Pu. Commercial radioactive sources for potential RDD include RTG (^{90}Sr), teletherapy and irradiators (^{60}Co and ^{137}Cs), industrial radiography (^{60}Co and ^{192}Ir), logging and moisture detectors (^{137}Cs, ^{241}Am and ^{252}Cf) (Hu et al. 2010).

3 Conventional Versus Phytoremediation Clean-up

The conventional remediation technologies, which are used for metal-polluted environments are in situ vitrification, soil incineration, excavation and landfill, soil washing, soil flushing, solidification, reburial of soil, stabilization of electrokinetic systems as well as pump and treat systems for water. When high radionuclide concentrations in soils pose risk to the environment, then two traditional soil treatments are usually used. Soil excavation is the first method, which removes the soil with radionuclides in its present state or after stabilization in concrete or glass matrices. However, this method is expensive as it requires packaging, transporting and disposal of contaminants (Ensley 2000; Negri and Hinchman 2000). This method only relocates the problem in the same proportion to a new location. The bulk density, soil compaction as well as aeration and water-holding capacity are affected due to heavy equipment's, which are used in soil excavation (Entry et al. 1997). Extra restoration applications are required to establish vegetation on such altered site (Huang et al. 1998). Another method involves soil washing, soil removal and chemical manipulations. Soil which is brought back after washing does not contain radionuclides, but is not thoroughly sterile with detergents, surfactants and chelating agents. If these chemicals leach into the ground water, they could pose more environmental problems (Entry et al. 1997). These technologies are too expensive, unsafe and inadequate and have a risk of releasing potentially harmful radionuclides into the atmosphere. Effectiveness and costs are also important for alternate remediation methods after ensuring public and ecosystem health. Environmental Protection Agency (EPA) requires, in order of preference suggests, that the nine criteria may be used to evaluate alternatives for remediation (Fig. 1).

Removal of toxic substances from the environment (soils) by using accumulator plants is the goal of phytoremediation. When decontamination strategies are impractical because of the size of the contaminated area, phytoremediation is advantageous. Due to the proven efficiency of phytoremediation, it draws great deal of interest from site owners, managers, consultants and contractors, in applying this technology to private, superfund and brown field sites. The success of phytoremediation depends upon the ability of a plant to uptake and translocate the contaminants (Chen et al. 2003). The ability of different plants to absorb radionuclides also depends on the environment and the soil properties (Entry et al. 1999). Recent studies have led to progressive insights into phytoremediation. The selection of an appropriate plant species is a crucial step (Huang et al. 1998), and screening of the suitable species involves complex studies (Mkandawire and Dudel 2005). The use of plant species for environmental clean-up of trace elements is based on their ability to concentrate element or radionuclide in their tissue (Zhu and Shaw 2000; Pratas et al. 2006). Successful utilization of phytoremediation technology involves analysis of factors governing the uptake, transportation and accumulation of metals in various plant parts (Diwan et al. 2010). High growth rate and biomass production are the desirable qualities for this process (Soudek et al.

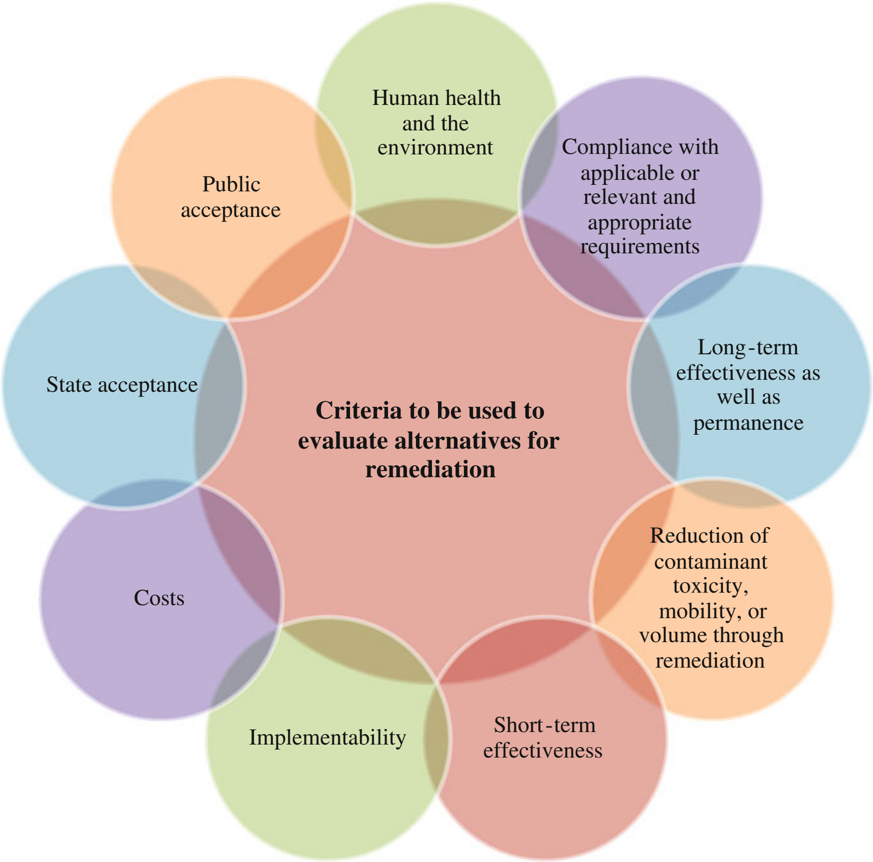

Fig. 1 Suggestions of Environmental Protection Agency (*EPA*) in order of preference that the nine criteria may be used to evaluate alternatives for remediation

2004; Cerne et al. 2010). Increasing metal accumulation in high-yielding crop plants without diminishing their yield is the most feasible strategy in the development of phytoremediation (Evangelou et al. 2007).

Willey and his colleagues (Broadley and Willey 1997; Willey and Martin 1997) have obtained relative radiocaesium uptake values in about 200 species and found that the highest values are all in the Chenopodiaceae or closely related families. Lasat et al. (1998) identified that red root pigweed (*Amaranthus retroflexus*) is an effective accumulator of radiocaesium which is capable of combining a high uptake of ^{137}Cs with high shoot biomass yield.

Hung et al. (2010) assessed the efficiency of vetiver grass for uranium accumulation and reported higher accumulation in lower fertile soils and more accumulation in roots in comparison with shoots. Štrok and Smodiš (2010) collected samples of plants from a uranium mill tailings waste pile containing ^{201}Pb, ^{226}Ra and ^{238}U and found that all radionuclides were highly accumulated in foliage, followed by shoots and wood, whereas Rodríguez et al. (2009) reported more U accumulated in leaves than fruits of some plant samples growing on a uranium mine. Sunflower (*Helianthus annuus* L.) and Indian mustard (*Brassica juncea* Czem.) are the most promising terrestrial candidates for metal (uranium) removal in water (Prasad and Freitas 2003). As discussed above, different plant species have different abilities to accumulate radionuclides from soil. While this variation has particular relevance in terms of being able to reduce the transfer of radionuclides from soil to food chains, it can also be exploited for the purpose of phytoremediation. However, with the present knowledge of plant uptake of radionuclides from soils, phytoremediation takes excessively long time. To speed up the process selection of suitable plant taxa, a special plant-breeding programme assisted by molecular biotechnology may be useful (Zhu and Shaw 2000).

4 Phytoremediation Techniques

The application of plants for environmental remediation requires the evaluation of a number of practical issues that have been divided into pre-harvest and post-harvest plans or strategies. Pre-harvest plan include the selection, design, implementation and maintenance of phytoremediation applications, whereas post-harvest strategies involve the disposal of plant and contaminant residues, which must also be taken into account fully during the design phase (Fig. 2). There are different techniques of phytoremediation (Table 2; Fig. 3) of toxic heavy metals and radionuclides from soil, groundwater, wastewater, sediments and brownfields (Zhu and Chen 2009; Sarma 2011; Ali et al. 2013).

4.1 Phytoaccumulation

It is also called as phytoextraction, phytoabsorption and phytosequesteration. It involves the uptake and translocation of metal contaminants from the soil by plant roots into the above ground parts of the plants (Chou et al. 2005; Eapen et al. 2006; Singh et al. 2009). Metal translocation to shoots is desirable in an effective process because generally the root biomass is not feasible (Singh et al. 2009; Tangahu et al. 2011). Certain plants called hyperaccumulators absorb unusually large amounts of metals in comparison with other plants. After the plants have been allowed to grow for several weeks or months, they are harvested and either incinerated or composted to recycle the metals. This procedure may be repeated as necessary to bring soil contaminant levels down to allowable limits (Horník et al. 2005).

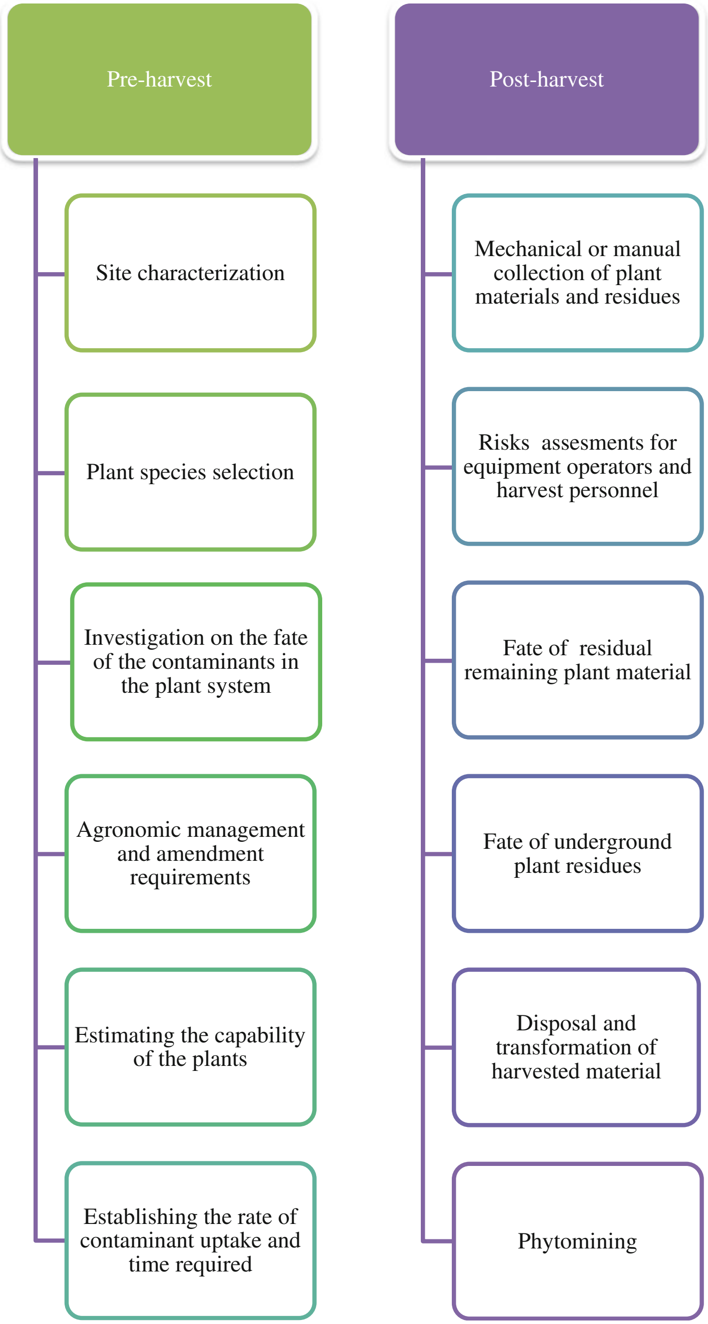

Fig. 2 Pre-harvest planning, implementation, maintenance issues and post-harvest strategies for effective phytoremediation

Table 2 Phytoremediation techniques and mechanisms for various heavy metals and radionuclides

Technique	Mechanism	Substrate	Heavy metals/radionuclides	Typical plant species
Phytoaccumulation	Hyperaccumulation	Soil, sediments	Cd, Cu, Ni, Pb, Zn, U, Cs, Sr	Indian mustard, rape seed, sunflower, Amaranthus, barley, maize
Phytofiltration	Root accumulation	Waste water, ground water	Cd, Cu, Ni, Pb, Zn Some radionuclide such as Cs, Sr, U and organic compounds	Algal spp., stonewort, hydrilla, water lens, catninetail, pondweed (Potamogeton, Chara)
Phytostabilization	Absorption/adsorption/ precipitation/ complexation	Soil, sediments	As, Cd, Cu, Zn, Cr, Pb, Se, U Hydrophobic organics	Phreatophyte trees, members of Poaceae with fibrous roots
Phytodegradation	Degradation in the plant	Soil, waste water, ground water	Herbicides, aromatics, chlorinated aliphatics, ammunition wastes	Poplar, willow, cottonwood, sorghum, rye, cowpea, alfalfa
Rhizodegradation	Breakdown by plant roots through microbial activity	Soil, sediments, waste water	Pesticides, aromatic hydrocarbons, polynuclear aromatic hydrocarbons	Apple, mulberry, rye fescue, Bermuda grass
Phytovolatilization	Volatilization by above ground parts	Soil, sediments, ground water	As, Hg, Se, tritium	Chinese brake, Indian mustard, poplar, canola, tobacco

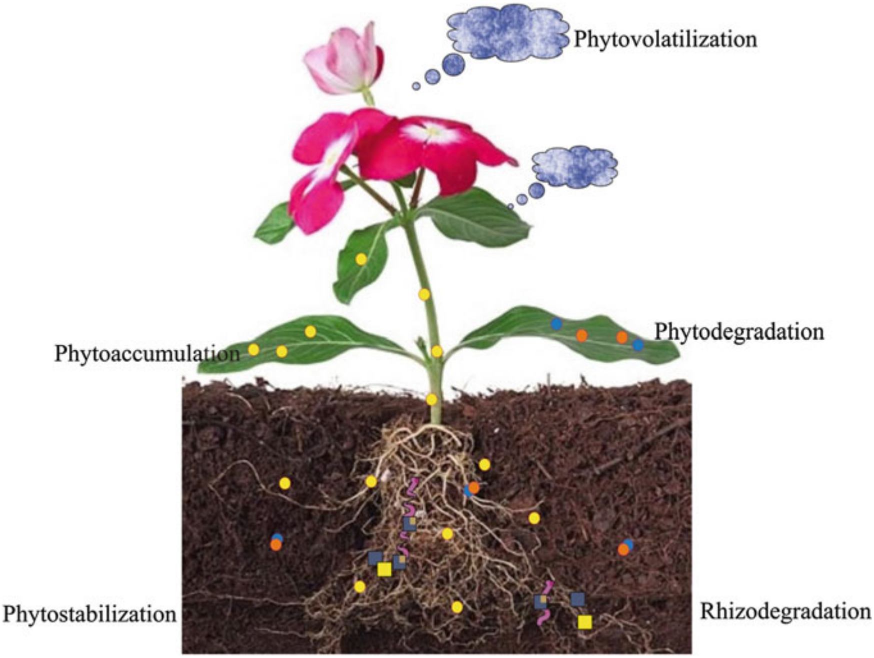

Fig. 3 Conceptual model showing various phytoremediation techniques

4.2 *Phytofiltration*

It is the exclusion of pollutants from contaminated surface waters or waste waters through plants. Phytofiltration may be categorized as blastofiltration (seedlings), caulofiltration (plant shoots) and rhizofiltration (plant roots) depending upon application of plant organ (Ali et al. 2013). During this process, absorption or adsorption of contaminants occurs, which minimizes their movement to underground waters (Ali et al. 2013). Rhizofilteration is the adsorption or precipitation on to plants roots or absorption of contaminants into the roots that are in solution surrounding the root zone. The plants to be used for clean-up are raised in green houses with their roots in water rather than in soil. To acclimatize the plants once a large root system has been developed, contaminated water is collected from a waste site and brought to the plants where it is substituted for their water source. The plants are then planted in the contaminated area where the roots take up the water and the contaminants along with it. As the roots become saturated with contaminants, they are harvested and either incinerated or composted to recycle the contaminants (Singh et al. 2009; Pratas et al. 2012).

4.3 Phytostabilization

It exploits certain plant species to immobilize contaminants in the soil and ground water through absorption and accumulation by roots, adsorption on to roots or precipitation within the root zone, complexation within rhizosphere (Wuana and Okieimen 2011; Singh 2012). Extended and abundant root system is a must to keep the translocation of metals from roots to shoots as low as possible (Mendez and Maiter 2008). This process reduces the mobility of the contaminant and prevents migration of contaminants to the ground water or air, and it reduces bioavailability for entry into the food chain (Erakhrumen 2007). This technique can be used to re-establish a vegetative cover at sites where natural vegetation is lacking due to high metal concentration in surface soils or physical disturbances to surficial materials. Tolerant species can be used to restore vegetation to the sites, thus decreasing the potential migration of contamination through wind erosion, leaching of soil and contamination of ground water (Dary et al. 2010; Manousaki and Kalogerakis 2011). By secreting certain redox enzymes, plants convert hazardous metals to a relatively less toxic state and decrease possible stress and damage (Ali et al. 2013).

4.4 Phytodegradation

It is also called as phytotransformation, which is the breakdown of organic contaminants or pollutants with the help of certain enzymes, e.g. dehalogenase and oxygenase. Phytodegradation is independent of rhizospheric microorganisms (Vishnoi and Srivastava 2008). Plants can uptake organic xenobiotics from contaminated environments and detoxify them through their metabolic activities. Phytodegradation is restricted to the removal of organic contaminants and cannot be applicable to heavy metals as they are non-biodegradable (Ali et al. 2013).

4.5 Rhizodegradation

It is also known as enhanced rhizosphere biodegradation, phytostimulation or plant-assisted bioremediation/degradation, which is the breakdown of contaminants in the soil through microbial activity in the presence of the rhizosphere (Mukhopadhyay and Maiti 2010). It is a much slower process than phytodegradation. Natural substances released by the plant roots—sugars, alcohols and acids—contain organic carbon, amino acids, flavonoids, that provides carbon and nitrogen sources for soil microorganisms, and creates a nutrient-rich environment. Certain microorganisms can digest organic substances such as fuels or solvents that are hazardous to humans and break down them into harmless products through biodegradation. Certain microorganisms can facilitate the oxidation of Fe^{2+} to Fe^{3+}. The Fe^{3+} ion, in turn, can convert insoluble uranium dioxide to soluble $(UO_2)^{2+}$ ions. This reaction enhances the mobility of uranium in soil from mining and milling wastes (Jagetiya and Sharma 2009).

4.6 *Phytovolatilization*

It is the uptake and transpiration of contaminants by plants, their conversion to volatile form with release of the contaminants or a modified form of the contaminant into the atmosphere. It does not remove the pollutant thoroughly; therefore, there are chances of its redeposition. Several controversies are there with this technique (Padmavathiamma and Li 2007). This process is used for removal of organic pollutants and heavy metals such as Se and Hg (Ali et al. 2013).

5 Plant Categorization According to Heavy Metals or Radionuclides Response

Plants show avoidance and tolerance strategies towards contaminants and based on this plants may be classified as indicators, excluders, accumulators and hyperaccumulators.

5.1 *Indicators*

Plants in which uptake and translocations reflect soil metal concentration with visible toxic symptoms are known as indicators. These plants generally reflect heavy metal/radionuclide concentration in the substrate. Metal indicators are species characteristic for soil contamination with specific metals. *Tradescantia bracteata* indicate radionuclides presence in the substrate (Prasad 2004).

5.2 *Excluders*

Plants that restrict the uptake of toxic metals into above ground biomass are known as excluder. Excluder plant has high levels of heavy metals in the roots and shoot/root ratio are less than one. These plants have low potential for extraction but are useful for phytostabilization purposes to avoid further contamination (Lasat 2002). According to Burger et al. (2013) *Plantago major* is an excluder plant particularly for U.

5.3 Accumulators

Accumulator plants reflect background metal concentrations by uptake and translocation of contaminants without showing visible toxicity signs. Metals are sequestered into the leaf epidermis, old leaves, epidermal secretory cells, in vacuoles and cell walls. Examples of accumulator plants are *Brassica campestris*, *Picea mariana* for U and *Festuca arundinacea* for ^{137}Cs and ^{90}Sr (Entry et al. 1997; Negri and Hinchman 2000; McCutcheon and Schnoor 2003).

5.4 Hyperaccmulators

The standard for hyperaccumulator has not been defined scientifically; however, hyperaccumulators species are capable of accumulating metals at levels 100-fold greater than those measured in common plants. The term ‘hyperaccumulator’ was first coined by Brooks et al. (1977). More than 500 plant species have been reported for their ability of heavy metal hyperaccumulation (Sarma 2011; Bulak et al. 2014), which includes members of the Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae and Lamiaceae families (Padmavathiamma and Li 2007). Literature shows that about 75 % of the species are Ni-hyperaccumulators (Prasad 2005). Some plants have natural ability of hyperaccumulation for certain heavy metals; these are known as natural hyperaccumulators, while the accumulation capacity of various plant species can be enhanced through soil amendments and genetic modification. Huang et al. (1998) reported that *Brassica juncea*, *Brassica narinosa, Brassica chinensis and Amaranth* sp. had more than 1,000-fold citric acid-triggered U hyperaccumulation. Members of family Brassicace, *Thlaspi caerulescens* and *Amaranth retroflexus* are found as hyperaccumulators of Co and Sr (McCutcheon and Schnoor 2003). Li et al. (2011) performed studies for the analysis of concentrations of U, Th, Ba, Ni, Sr and Pb in plant species collected from uranium mill tailings. The removal capability of a plant for a target element was assessed. Out of the five plant species, *Phragmites australies* had the greatest removal capabilities for uranium (820 μg), thorium (103 μg) and lead (1,870 μg). Eapen et al. (2006) designate *Calotropis gigantea* (giant milky weed) as a potential candidate to remove ^{137}Cs and ^{90}Sr from soils as well as solutions.

6 Improved Phytoremediation

In order to increase the efficiency of phytoremediation technologies, it is important that we must learn more about different biological processes involved. These include plant–microbe interactions, rhizosphere processes, plant uptake, translocation mechanisms, tolerance mechanisms and plant chelators involved in storage and transport. Research on the movement of contaminants within the ecosystems via soil–water–plant system to higher trophic levels is also necessary (Pilon-Smits 2005).

Several approaches may be applied to further enhance the efficiency of metal phytoremediation. All of the above, a screening study may be performed to identify the most suitable plant species for remediation. Second, agronomic practices may be optimized for a selected species to maximize biomass production and metal uptake (Chaney et al. 2000). Amendments such as organic acids or synthetic chelators may be added to soil to accelerate and increase metal uptake (Blaylock and Huang 2000). Spatial and successful combination of different plant species assures maximal phytoremediation efficiency (Horne 2000).

Agronomic practices such as fertilization, addition of vermicompost and plant clipping may also affect plant metal uptake by influencing microbial density and composition of the root zone. Further breeding of selected species can be done for the desired property, either through classic breeding or via genetic engineering. Considerable progress had been made in unrevealing the genetic secrets of metal-eating plants. Metal hyperaccumulator genes have been marked and cloned (Moffat 1999; Macek et al. 2008). These will identify new non-conventional crops, metallocrops that can decontaminate metals in the environment (Ebbs and Kochian 1998).

6.1 Chemically Induced Phytoremediation

Chemically induced phytoremediation makes use of natural and synthetic chelators that enhance the mobility of metals by adding them in soil (Marques et al. 2009; Marchiol and Fellet 2011). In late 1980s and early 1990s, ethylenediaminetetra-acetic acid (EDTA) was suggested as a chelating agent for the assistance of phytoaccumulation. The influence of EDTA has ranged from non-significant to over 100-fold enhanced accumulation of heavy metals (Grčman et al. 2001). Nitrilotriacetic acid (NTA) is a chelating agent, which has been used in the last 50 years primarily in detergents. The influence of addition of NTA on the mobilization and uptake of heavy metals was observed in various studies (Chiu et al. 2005; Quartacci et al. 2005). Natural low molecular weight organic acids (NLMWOAs), such as citric acid (CA), oxalic acid (OA) or malic acid, because of their complexing properties, are of particular importance and play a significant role in heavy metal solubility, plant uptake and accumulation (Qu et al. 2011; Jagetiya and Sharma 2013). Both synthetic and natural chelators can desorb metals from the soil matrix to form water-soluble metal complexes into the soil solution (Quartacci et al. 2005; Saifullah et al. 2010). There are few limitations to the use of complexing agents. Many synthetic chelators, such as EDTA, Ethylenediamine-N,N′-disuccinic acid (EDDS) have low degree of biodegradability (Jiang et al. 2003; Wu et al. 2005; Bianchi et al. 2008; Dermont et al. 2008). This problem may be overcome by usage of low phytotoxic and easily biodegradable compounds such as NTA and NLMWOAs (Chen et al. 2003; Wenger et al. 2003), which are more effective in increasing the metal solubility (Vamerali et al. 2010; Rahman and Hasegawa 2011).

Radionuclides existing in soil can be dissolved in solution, complexed with soil organics, precipitate as pure or mixed solids and ion-exchanged in reaction (Gavrilescu et al. 2009). For moderately polluted soils, in situ phytoremediation (Behera 2014) is an eco-friendly but time-requiring solution (Evangelou et al. 2007; Jensen et al. 2009). The order for complexation of heavy metals with different complexing agents in soils occurs in the following order, EDTA and related synthetic chelators > NTA > citric acid > oxalic acid > acetic acid, which was shown by many comparative experiments (Krishnamurti et al. 1997; Wenger et al. 1998; Jagetiya and Sharma 2013). Enhanced uranium accumulation through EDTA has also been reported by (Hong et al. 1999; Sun et al. 2001). Huang et al. (1998) proposed that citric acid was the most effective of some organic acids (acetic acid, citric acid and malic acid) tested in enhancing uranium accumulation in plants. Shoot uranium concentration of *B. juncea* and *B. chinensis* grown in uranium-contaminated soil (total soil uranium, 750 mg kg^{-1}) increased from 5 to more than 5,000 mg kg^{-1} in citric acid-treated soils. This is the highest shoot uranium reported for plants grown on uranium-contaminated soils.

Applications of chelating agents, such as citric acid, oxalic acid, EDTA, cyclohexylene dinitrilo tetraacetic acid (CDTA), diethylene triamine pentaacetic acid (DTPA), and NTA, have been tested by many researchers (Sun et al. 2011; Jagetiya and Sharma 2013; Oh et al. 2014). Synthetic chelators are non-biodegradable and can leach into underground water supplies making an additional environmental problem. Furthermore, synthetic chelators can be toxic to plants at higher concentrations. Therefore, proper measures should be followed while practicing induced phytoextraction (Marques et al. 2009; Zhuang et al. 2009; Zhao et al. 2011; Song et al. 2012). However, use of citric acid as a chelating agent could be promising because it has a natural origin and is easily biodegraded in soil. Its non-toxic nature does not hamper plant growth (Smolinska and Krol 2012; Ali et al. 2013).

6.2 Phytoremediation Through Microorganisms

Among the microorganisms, algae are of predominant interest of the ecological engineer as they can live under many extreme environments. Once induced to grow in waste waters, they would provide a simple and long-term means to remove radionuclides from the mining effluents. According to a study performed by Kalin et al. (2004), some algal forms possess the quality to sequester U from the contaminated sites. Fukuda et al. (2014) examined 188 strains from microalgae, aquatic plants and unidentified algal species that can accumulate high levels of radioactive Cs, Sr and I from the medium.

In order to understand the radionuclide cycling and dispersal, the effects of bioaccumulation by bacteria or fungi must be acknowledged. The symbiotic relationships can lead to radionuclide uptake by the vascular plant hosts (Shaw and Bell 1994). In the experiments performed by Horak et al. (2006), a new biosorption material, called biocer, was used, which consists of a combination of a biological component with ceramic material. The bacterial strain used for this purpose was *Bacillus sphaerius*, which is known for its excellent sorption capacity of U and other heavy metals.

Tsuruta (2004) examined the cell-associated adsorption of Th and U from the solution by using various microorganisms. Those with high Th adsorption abilities were exhibited by strains of the gram-positive bacteria *Arthrobacter nicotianae* IAM12342, *Bacillus subtilis* IAM1026, *Bacillus megaterium* IAM1166, *Micrococcus luteus* IAM1056, *Rhodococcus erythropolis* IAM1399 and *Streptomyces levoris* HUT6156, and high U adsorption abilities were noticed in some gram-positive bacterial strains *S. albus* HUT6047, *S. levoris* HUT6156 and *A. nicotianae* IAM12342.

Lichens can occur in extreme metalliferous environments and can accumulate high amounts of potentially toxic metals (Richardson 1995). They can be used for biomonitoring U discharge from mining activities and radionuclide fallout from nuclear weapon testing and nuclear accidents (Feige et al. 1990). McLean et al. (1998) suggested U adsorption to melanin-like pigments in the outer apothecial wall of the lichen *Trapelia involuta*. The relationships between U, Cu and Fe and the melanin-like pigments in fungal hyphae suggest that the pigments in the exciple and epithecium have a high probability related to the metal accumulation (Takeshi et al. 2003).

Arbuscular mycorrhiza (AM), protect host roots from pathogens, assist in uptake of heavy metals and radionuclides (Selvaraj et al. 2004, 2005).The assistance of AM fungi and the soil's nature to hold the radionuclide to prevent the expression of radioactivity provides greater chances for the vegetation's to survive in the disturbed ecosystem in a better way. Selvaraj et al. (2004) hold a view that due to strong circumstantial evidence, AM fungi would enhance uptake and recycling of radionuclides particularly ^{137}Cs and ^{90}Sr. According to Declerck et al. (2003), mycorrhizal fungi have also been observed to enhance acquisition of ^{137}Cs and Entry et al. (1999) observed the same for ^{90}Sr. In a study performed by Chen et al. (2005), the effects of the mycorrhizal fungus *Glomus intraradices* on U uptake and accumulation by *Medicago truncatula* L. were studied and it was found that such mycorrhiza-induced retention of U in plant roots may contribute to the phytostabilization of uranium-contaminated environments.

Excellent biosorption ability in fungi and yeast are from genera of *Aspergillus, Rhizopus, Streptoverticullum* and *Sacchromyces* (Akhtar et al. 2013). Plant growth promotion and detoxification of hazardous compounds occur in rhizosphere (Epelde et al. 2010). The cooperation between plants and beneficial rhizosphere microorganisms can upgrade the tolerance of the plants to heavy metals, thus making the microorganisms an important component of phytoremediation technology (Melo et al. 2011).

Microorganisms may directly reduce many highly toxic metals (e.g. Cr, Hg and U) via detoxification pathways. Microbial reduction of certain metals to a lower redox state along with other metal precipitation mechanisms may result in reduced mobility and toxicity (Gadd 2008; Violante et al. 2010). Bioremediation technology utilizes various microorganisms or enzymes for the abolition of heavy metals from polluted sites (Gaur et al. 2014).

6.3 Phytoremediation Through Transgenic Plants

Genetic engineering can be implemented in improving phytoremediation capacity of plants (Wani et al. 2012). Transgenic approaches successfully employed to promote phytoextraction of metals (mainly Cd, Pb and Cu) and metalloids (As and Se) from soil by their accumulation in the aboveground biomass involves implementation of metal transporters, improved production of enzymes of sulphur metabolism and production of metal-detoxifying chelators. Phytovolatization of Se compounds was promoted in plants overexpressing genes encoding enzymes involved in production of gas methylselenide species (Kotrba et al. 2009).

Genetic studies on hyperaccumulators have been underway for many years (Whiting et al. 2004). Most of the studies have been carried out on the identification of genes involved in the process of hyperaccumulation, uptake, transport and sequestration (Rutherford et al. 2004). Van Huysen et al. (2003, 2004) have described transgenic plants with the ability to take up and volatilize Se.

Genetic engineering has provided new gateways in phytoremediation technology by offering the opportunity for direct gene transfer (Bhargava et al. 2014). This approach of the development of transgenic having increased uptake, accumulation and tolerance can be considered as a good alternative. Engineered plants and microbes are used to treat efficiently low to moderate levels of contamination (Behera 2014).The selection of ideal plant species for phytoremediation engineering is based upon production of high biomass, accumulation, tolerance and competitive and a good phytoremediation capacity (Doty 2008). The genes involved in metabolism, uptake or transport of specific pollutants can enhance the effectiveness of phytoremediation in transgenic plants (Cherian and Oliveira 2005; Eapen et al. 2006; Aken 2008). *Populus angustifolia, Nicotiana tabacum* and *Silene cucubalis* have been genetically engineered to overexpress glutamylcysteine synthetase and thus provide enhanced heavy metal accumulation as compared to a corresponding wild-type plant (Fulekar et al. 2009). At the same time, ecological, social and legal objections persist to the practical application of genetically modified organisms in the field. Thus, genetic strategies, transgenic plants, microbe production and field trials will fetch phytoremediation field applications (Pence et al. 2000; Krämer and Chardonnens 2001; Ali et al. 2013).

7 Metal Uptake, Translocation and Accumulation

The main steps during accumulation of metals in plants involve mobilization of metals, uptake from soil, compartmentation and sequestration, xylem loading, distribution in aerial parts and storage in leaf cells (Dalvi and Bhalerao 2013). At each step, concentration, selectivity of transport activities and affinities of chelating molecules affect metal accumulation (Clemens et al. 2002).

Root exudates of natural hyperaccumulators solubalize metals, which causes acidification of rhizosphere (Mahmood 2010) and leads to metal chelation by secretion of mugenic and aveic acid (Dalvi and Bhalerao 2013). The complete mechanism of whole process is unclear. Metal enters in plant either through intercellular spaces (apoplastic pathway) or by crossing plasma membrane (symplastic pathway) (Peer et al. 2006; Saifullah et al. 2009). Ghosh and Singh (2005) stated that inward movement of metals during symplastic pathway takes place due to strong electrochemical gradient.

The fate of metal after entry into roots can be either storage in the roots or translocation to the shoots primarily through xylem vessels (Jabeen et al. 2009) where they are stored in vacuoles as they possess low metabolic activities (Denton 2007). Sequestration in the vacuole removes excess metal ions from the cytosol and reduces their interactions with cellular metabolic processes (Sheoran et al. 2011).

Uranium uptake and accumulation were investigated in twenty different plant species by Soudek et al. (2011). They used hydroponically cultivated plants, which were grown on uranium-containing medium. *Zea mays* were found to have highest uptake, while *Arabidopsis thaliana* had the lowest. The amount of accumulated U was strongly influenced by U concentrate in the cultivation medium. U accumulated mainly in the roots.

Viehweger and Geipel (2010) conducted a comparative study of U accumulation and tolerance in terrestrial versus laboratory trials on *A. halleri*, which grew on U mining site. In the native habitat, the plant sequesters high amount of U in roots than shoots, but in hydroponic trails, roots accumulated 100-fold more and shoots accumulated tenfold more U. This drastic increase in U accumulation could be attributed to iron deficiency in hydroponic trials.

Due to the similar oxidation states and ionic radii, non-essential heavy metals compete and enter roots through the same transmembrane transporters used by essential heavy metals (Alford et al. 2010). Seth (2012) suggests that the relative lack of selectivity in ion transport may explain the reason of the entry of such metals.

8 Advantages and Limitations of Phytoremediation

Phytoremediation, which is also called as green remediation, botano-remediation, agroremediation or vegetative remediation is an emerging group of technologies utilizing green plants to clean up the environment from contaminants and has been offered as a simple and non-invasive alternative to the conventional engineering-based remediation methods (El-Gendy 2008; Vandenhove et al. 2009; Sevostianova et al. 2010; Hoseinizadeh et al. 2011). Soil is the ultimate and most important sink of chemical components in the terrestrial environment (Roy et al. 2010). Some of the advantages listed till date are (Negri and Hinchman 2000; Doty 2008; Lone et al. 2008) as follows:

- It is economically viable, aesthetically pleasing and easy to implement.
- It has the potential to treat sites polluted with more than one type of pollutant.
- During the whole process, plants serve as stabilizers, thus contaminants cannot escape into the neighbourhoods.
- The plants also provide the soil nutrients and stabilization by reducing wind and water erosion.
- Reduces the exposure time to the radionuclides.
- Easy monitoring of the sites with wildlife enrichment.
- No harm to the soil dynamics as the soil is treated in situ. A special advantage of phytoremediation is that soil functioning is maintained and life of soil is reactivated.
- Once plants are established, they remain for consecutive harvests to continually remove the contaminants.
- It has lower side effects than physical and chemical approaches.

  Despite of the above-mentioned advantages, it holds some limitations (Wu et al. 2005; Singh et al. 2007; Ali et al. 2013).
- It is applicable to sites with low to moderate levels of metal contamination because plant growth is not sustained in heavily polluted soils.
- Slow growth rate and low biomass of hyperaccumulators.
- It requires lot of time.
- Limited tolerance of the plant species.
- Tightly bound fraction of metal ions cannot be removed from soil due to limited bioavailability.
- Sometimes, the agro-climatic and hydrological conditions may limit the plant growth and there are chances of entering of the contaminants in food chain through animals/insects feeding on plant material loaded with contaminants.
- Lower efficiency over other non-biological remediation techniques and the limitations when the contaminated soil layer occasionally extends to the deeper profile.

9 Future Prospects of Phytoremediation

Phytoremediation is used for removal of variety of toxic metals and radionuclides, while minimal environmental disturbance and larger public acceptance (Liu et al. 2000; Tangahu et al. 2011; Fukuda et al. 2014). An easy handling of this technology shows its strong ability as a natural, solar energy-driven remediation approach for multiple pollutants (Singh et al. 2007). Phytoextraction using a combination of high biomass with hyperaccumulator mechanisms will successfully remove contaminants from the environment (Ali et al. 2013).

Phytoremediation field projects, proposed for the forthcoming time, should benefit from collaboration between research groups and industry so that they can be designed to address hypotheses and obtain scientific knowledge for clean-up standards. Phytoremediation is expected to be commercialized and used as a vital tool in sustainable management of contaminated soils, especially in developing countries which cannot afford sophisticated technologies due to their vast populations (Mirza et al. 2014). Bioavailable fraction of the pollutant should be the focal point in order to reduce the costs and enable the clean-up of sites with the limited funds (Pilon-Smits 2005).

As the mixtures of organic as well as inorganic pollutants occur in 64 % of polluted sites (Ensley 2000), phytoremediation can be helped by more collaborative studies by teams of researchers from different backgrounds. In general, the advantages and limitations of phytoremediation must be accessed for a particular project to determine whether this type of remediation is the most appropriate for the task. Several hyperaccumulator plants remain to be discovered or recognized, and we need to acquire more information about their physiology (Raskin et al. 1994).

Further, research on easily biodegradable chemicals in phytoremediation process is still required before the safe adoption of this technology in fields (Luo et al. 2006). The use of easily biodegradable chelating agents (Tandy et al. 2006) enhances the process of phytoextraction (Evangelou et al. 2007) and reduces the remediation time period. There is a necessity of optimization of the process, proper understanding of the mechanism of uptake and proper disposal of biomass produced. Several methods regarding plant disposal have been described but data are scarce (Ghosh and Singh 2005).

In-depth research of cellular mechanisms involved in heavy metal avoidance, uptake, transport and accumulation is essential (Dalvi 2013). Investigations are being done to identify and characterize several proteins involved in cross-membrane transport and vacuole sequestration of heavy metals. Molecular advancement and achievements in such studies will greatly help in unrevealing the mechanism as well as enhancing the efficiency of phytoremediation (Ali et al. 2013).

In times to come, mining of genomic sequences from *A. thaliana* and rice and availability of new genetic technologies should lead to the identification of novel genes important for pollutant remediation and tissue specific transporters. Challenging issues such as biosafety assessment and genetic pollution involved in adopting the new initiatives for cleaning up the polluted ecosystems must not be ignored, from both ecological and greener point of view (Mani and Kumar 2013). Laboratory studies on the potential of transgenic plants and/or microbes to remediate organic and inorganic contaminants are to be further explored (Doty 2008).

The future of phytoremediation consists of ongoing research work and has to pass through a development phase, and there are several technical barriers, which need to be addressed. We still need to completely understand the ecological complexities of the plant–soil interactions. We should soon be able to shed light on some of the poorly understood phenomena related to the extensive field of phytoremediation. This area of research deserves multidisciplinary (soil chemistry, plant biology, ecology and soil microbiology as well as environmental engineering) investigations using molecular, biochemical and physiological techniques (Khan 2006). Heavy metal detoxification can be achieved by optimization of plants through multidisciplinary approach. Phytoremediation of multiple contaminated sites is urgently required along with increasing its scope and efficiency (Oh et al. 2014). We need to optimize the agronomic practices, better plant-microbe combinations and plant genetic abilities in order to develop commercially useful practice (Jagetiya and Sharma 2009; Oh et al. 2014).

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Natural Plant Selection for Radioactive Waste Remediation

Nan Hu, Dexin Ding and Guangyue Li

Abstract Phytoremediation of radioactive waste is a process that uses plants to remove, transfer, or immobilize radionuclides from the contaminated soil, sediment, sludge, or water, and it is a useful method for treating large-scale low-level radionuclide contamination. However, there have not been established criteria which can be utilized to screen out suitable plant species that are capable of remediating the radioactive waste. In this chapter, important factors influencing the selection of natural plant to remediate radioactive waste, including the characteristics of radioactive waste, the vegetation plant species and vegetation community composition in the radioactive waste deposited area, the concentration of a target radionuclide in the plant, the biomass of the plant, and the concentration of a target radionuclide in the radioactive, are analyzed, and the criteria based on the phytoremediation factor (PF) have been proposed for the selection of natural plant to remediate radioactive waste.

Keywords Phytoremediation · Radionuclide · Radioactive waste · Plant screening · Hyperaccumulator

Contents

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1 Introduction

In the present chapter, radioactive waste mainly refers to radionuclide-contaminated soil, sediment, sludge, and water. The mechanisms of phytoremediation applicable to radioactive waste include enhanced rhizosphere biodegradation, phytoextraction, phytodegradation, and phytostabilization. Because radionuclides cannot be biodegraded, the mechanisms applicable to remediation of radionuclides are phytoextraction and phytostabilization. Phytoextraction is a process that includes the uptake of radionuclides by plant roots from the contaminated soil and the translocation/accumulation of radionuclides into plant shoots and leaves. The plants are subsequently harvested from the growing area, dried, and disposed of. Phytostabilization involves the production of chemical compounds by plants and their immobilization of radionuclides on the interface between roots and radioactive waste. Radionuclides transport in soil, sediments, or sludges can be reduced through absorption and accumulation by the plant roots; adsorption onto roots; precipitation, complexation, or metal valence reduction in soil within the root zone; or binding to humic (organic) matter through the process of humification. Before phytoremediation can be applied for remediating radioactive waste, the appropriate natural plant species should be selected. The procedures for screening the suitable plant species for phytoremediation of radioactive waste are as follow: First of all, the characteristics of radioactive waste to be remediated should be analyzed; secondly, the vegetation plant species and vegetation community composition in the radioactive waste deposited area should be surveyed; thirdly, the concentration of a target radionuclide in the plant should be determined; fourthly, the biomass of the plant should be calculated; and finally, the concentration of a target radionuclide in the remediated radioactive waste should be measured.

In this chapter, based on the previous work on screening of plant species for phytoremediation of U, Th and ^{226}Ra-contaminated soils from uranium mill tailings impoundment in South China, important factors influencing the selection of natural plant for the remediation of radioactive waste were analyzed, and the criteria based on the phytoremediation factor (PF) were proposed for the selection of natural plant to remediate radioactive waste.

2 Characteristics of Radioactive Waste

The characteristics of radioactive waste are important factors to be considered in selecting the natural plant species for phytoremediation, since they will impact the growth of the candidate for phytoremediation of the radioactive waste. Based on the characteristics of radioactive waste, preliminary treatments, such as adjusting pH value for plant growth, supplying fertilizer to improve the physicochemical properties of radionuclides, and adding the chelating agent to increase the bioavailability of radionuclides in the radioactive waste, could be conducted.

In this chapter, the candidates for phytoremediation of radioactive waste were selected from the natural plants growing in a uranium mill tailings impoundment in South China. The impoundment has a subtropical continental climate with an annual average temperature of 17.9 °C, an annual average rainfall of 1452.0 mm, and an annual average evaporation capacity of 1324.5 mm, and its altitude is from 210.5 to 307.0 m above sea level. It covers an area of approximately 1.70 km^2 and contains approximately 1.88×10^8 t of uranium mill tailings produced by a nearby uranium mill where the uranium ore was processed by acid leaching from 1963 to 1994. The tailings were sandy and without any nutrients and organic matter when they were deposited initially. But at present, on the top of the uranium tailings, many scattered regolith layers in thickness of 1–2 cm with high nutrient content or organic material from the rotten plants have been formed, and many plant species have colonized in the regolith layers.

The characteristics of the uranium mill tailings in the impoundment are presented in Table 1. The particle sizes of the tailings collected from the uranium mill tailings impoundment ranged between 0.040 and 0.074 mm. The pH value of the tailings ranged from 4.42 to 6.10. The reason for this was that the uranium ore was processed by acid leaching in the former uranium ore reprocessing factory and that the uranium mill tailings impoundment was in an acid rain zone (Fan et al. 2010). In this acidic environment, the mobility of the hazardous materials including radionuclides and heavy metals will increase. It was obvious that there was a great difference between the minimum and maximum values of the concentrations of the determined elements in the tailings. Three explanations for this may be given. First, the tailings had the acidic nature, this resulted in the dissolution of the elements from the tailings, and they could flow with the rainfall from one site to another. Second, the tailings had been deposited at the impoundment during different periods from 1963 to 1994, and this resulted in the different releasing order of the elements. Third, different plant species had different uptake activities for the elements from the tailings. The uranium mill tailings also contained considerable nutrients and trace elements needed for growth of plants.

Phytoremediation is limited to shallow soils and sediments. Because the growth of plants used in phytoremediation can be affected by climatic or seasonal conditions (FRTR 2002), this technology may not be applicable in areas with cold climates and short growing seasons.

Table 1 Characteristics of the tailings deposited in the uranium mill tailings impoundment in South China (Li et al. 2011; Hu et al. 2014)

Mill tailings characteristics	
Grain size	0.040–0.074 mm
pH	4.42–6.10
SiO_2	70.65–74.89 %
Fe	1.80–2.10 %
Al	2.85–3.25 %
Ca	3.35–3.56 %
Mg	0.14–0.17 %
P	0.0012–0.093 %
K	0.0027–0.0052 %
B	0.0008–0.0012 %
Mo	0.0063–0.0071 %
Cl^-	0.024–0.031 %
SO_4^{2-}	0.026–0.035 %
NO_3^-	0.28–0.32 %
Total C	2.86–4.52 %
CEC	8.65–9.87 cmol kg^{-1}
U	6.03–46.5 μg g^{-1}
Th	4.75–19.8 μg g^{-1}
^{226}Ra	7.32–29.52 Bq g^{-1}

3 Vegetation Plant Species and Vegetation Community Composition in the Radioactive Waste Deposited Area

The vegetation plant species and vegetation community composition in the radioactive waste deposited area are important for selecting the natural plant species for phytoremediation of radioactive waste. The selected plant species should be the dominant species, since they will cause the minimal impact on the ecological interaction between the local plants and keep the stability of the vegetation community.

An extensive survey was conducted in autumn 2011. To survey the vegetation composition of the flora in the mill tailings impoundment, 9 sampling sites were selected systematically in the uranium mill tailings impoundment (S1–S9, Fig. 1). Six sampling sites were in the dump 1, and the other three sampling sites were in dump 2.

In total, 80 species were recorded in the sampling sites. They belonged to 67 genera in 32 families (Table 2). Most of the species recorded were perennial forbs and grasses. The Poaceae and Asteraceae were the dominant families colonizing the impoundment and had 16 and 13 species, respectively, the Rosaceae and Cyperaceae had 5 species each, and the rest had less than 3 species. There were also some trees, including *Broussonetia papyrifera*, *Paulownia fortunei*, *Cinnamomum camphora*, *Salix matsudana*, *Rhus chinensis,* and *Melia azedarach*. Based on the life-form, most of the species were shallow-rooted, drought-tolerant plants and belonged to common native plants. In terms of the composition of vegetation

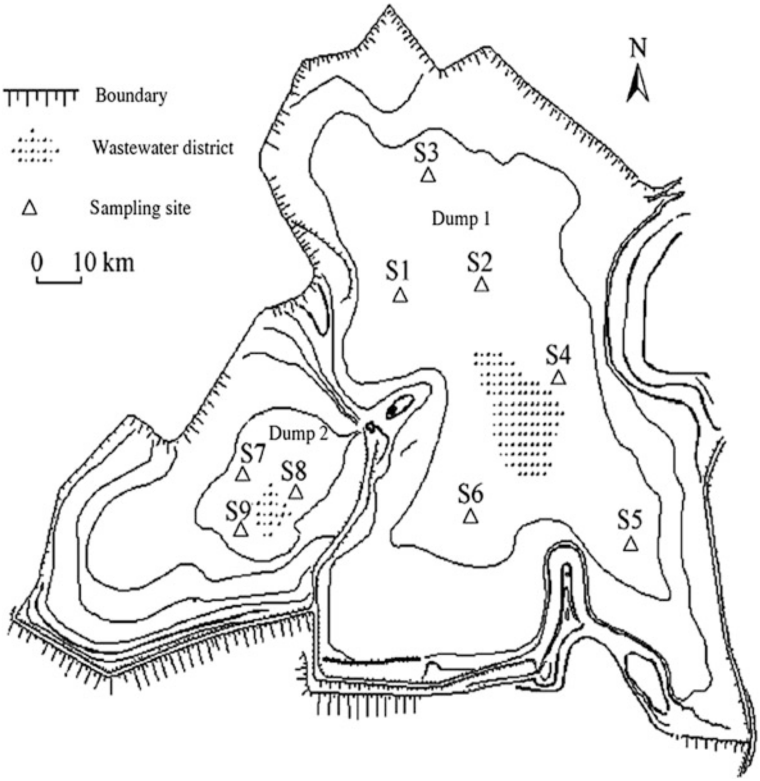

Fig. 1 Distribution of the sampling sites in the uranium mill tailings impoundment in South China (Hu et al. 2014)

community and the life-form, most of the species recorded were 1-year or 2-year perennial herbs, with a small number of trees and shrubs. The trees grew in the impoundment mainly belonged to typical positive pioneer plants.

In the investigation, only 7 species (*Kyllinga brevifolia, Phragmites australis, Imperata cylindrica, Setaria viridis, Pteris multifida, Pteris cretica L. var. nervosa,* and *Pteridium aquilinum*) occurred in all the sampling sites. Furthermore, 12 species, including *Oxalis corymbosa, Avena fatua, Paspalum scrobiculatum, Eleusine indica, Miscanthus floxidulus, Polypogon fugax, Erigeron annuus, Erigeron canadensis, Solanum nigrum, Trema dielsian, R. chinensis,* and *Dryopteris scottii*, occurred in 8 sampling sites. However, there were 13 species including *Persicaria hydropiper, P. fortunei, C. camphora, Cyperus difformis, Rubus alceaefolius, Digitaria sanguinalis, Herba taraxaci, S. matsudana, Amaranthus spinosus, Plantago asiatica, Plantago major, Boehmeria nivea,* and *Medicago sativa* occurring only in sampling sites.

The vegetation composition was influenced by grazing pressure, age of enclosures, and seasonality (Fernandes et al. 2006; Angassa and Oba 2010). Three types

Table 2 Plant community composition on the sampling sites at uranium mill tailings impoundment in South China (Hu et al. 2014)

Family	Species	Abundance[a]								
		S1	S2	S3	S4	S5	S6	S7	S8	S9
Moraceae	*Morus alba*	0	0	1	2	1	0	0	3	0
	Broussonetia papyrifera	0	0	3	5	2	2	0	4	4
	Humulus scandens	0	1	0	4	0	0	0	3	3
Polygonaceae	*Polygonum posumbu*	0	0	2	1	2	1	0	0	2
	P. lapathifolium	0	1	1	2	0	2	0	2	2
	P. hydropiper	0	0	1	0	2	0	0	0	1
Scrophu lariaceae	*Paulownia fortunei*	0	0	1	0	0	0	0	1	2
Lauraceae	*Cinnamomum camphora*	0	0	0	1	0	0	0	1	2
Oxalidaceae	*Oxalis violacea*	1	0	0	1	1	2	1	0	0
	O. corymbosa	1	1	3	4	2	3	0	4	3
Verbenaceae	*Vitex negundo*	0	0	0	4	1	1	0	2	3
	Clerodendrum cyrtophyllum	0	0	3	2	4	3	0	3	3
Cyperaceae	*Kyllinga brevifolia*	1	1	2	4	1	1	1	2	3
	Juncellus serotinus	1	0	2	3	1	1	0	2	2
	Cyperus iria	0	0	2	3	2	0	1	3	4
	C. difformis	0	0	0	1	0	0	1	2	0
	Cyperus rotundus	0	1	3	4	2	2	0	3	4
Rosaceae	*Duchesnea indica*	0	1	0	1	2	1	0	1	0
	Rosa laevigata	0	0	0	2	0	1	1	0	1
	Rubus corchorifolius	0	0	1	0	2	0	2	1	0
	R. alceaefolius	0	0	0	1	0	1	0	0	1
	R. hanceanus	0	1	1	3	3	4	1	2	4
Phytolaccaceae	*Phytolacca acinosa*	0	0	2	0	2	2	0	5	5
Portulacaceae	*Portulaca oleracea*	0	0	2	1	2	1	0	0	2
Poaceae	*Avena fatua*	1	1	2	4	0	2	1	4	4
	Alopecurus aequalis	0	1	0	0	0	1	0	3	4
	Digitaria sanguinalis	0	0	0	0	1	0	0	3	2
	Phragmites australis	3	4	1	2	3	2	4	2	2
	Paspalum scrobiculatum	2	2	1	2	2	2	1	3	0
	P. distichum	0	2	1	0	2	1	0	2	3
	Potamogeton pectinatus	0	0	2	1	2	1	0	1	1
	Poa pratensis	0	0	2	1	2	1	0	3	4
	Rhizoma imperatae	0	0	1	2	0	0	0	1	2
	Imperata cylindrica	2	4	1	2	2	2	4	2	3
	Eragrostis pilosa	0	1	3	2	2	3	0	2	3
	Eleusine indica	1	0	2	1	3	1	2	3	3
	Miscanthus floxidulus	2	1	3	3	5	5	1	3	0
	Phleum alpinum	0	1	1	2	2	2	0	2	2
	Polypogon fugax	1	0	3	2	1	1	1	2	3
	Setaria viridis	2	4	2	2	2	1	4	3	2

(continued)

Table 2 (continued)

Family	Species	Abundance[a]								
		S1	S2	S3	S4	S5	S6	S7	S8	S9
Asteraceae	*Artemisia lavandulaefolia*	1	0	1	3	2	1	0	1	1
	Artemisia capillaris	1	0	2	3	1	3	1	3	4
	Bidens pilosa	0	0	0	1	2	0	0	3	3
	Erigeron annuus	1	1	2	4	2	3	0	2	2
	E. canadensis	1	0	2	1	2	3	1	3	2
	E. sonchifolia	1	0	0	4	1	1	0	1	1
	Herba taraxaci	0	0	0	1	0	1	0	0	1
	H. gnaphaii	0	0	3	1	4	1	0	2	2
	Ixeris chinensis	0	0	2	0	3	2	3	2	3
	Senecio scandens	0	0	1	2	3	2	0	0	2
	Gynura crepidioides	0	0	2	0	0	1	0	1	1
	Youngia japonica	0	0	1	2	2	0	0	0	1
	Xanthium sibiricum	0	0	1	3	1	0	0	2	2
Solanaceae	*Solanum nigrum*	0	2	3	1	3	2	1	3	3
	S. lyratum	0	0	2	2	0	0	0	1	1
Ulmaceae	*Trema dielsian*	1	0	2	3	2	3	2	3	3
	Ulmus parvifolia	0	0	2	1	1	0	0	1	2
Hamamelidaceae	*Loropetalum chinense*	0	0	1	4	1	1	0	4	5
Liliaceae	*Smilax china*	0	0	1	1	0	0	0	1	1
Salicaceae	*Salix matsudana*	0	0	0	0	0	0	0	1	1
Oleaceae	*Ligustrum quihoui*	0	0	0	1	0	1	0	1	1
Amaranthaceae	*Amaranthus spinosus*	0	0	0	1	0	0	0	2	1
	Alternanthera philoxeroides	0	0	0	2	1	1	0	1	1
Euphorbiaceae	*Ricinus communis*	0	0	1	1	2	2	0	3	4
	Mallotus apelta	1	3	0	2	3	3	1	2	0
Anacardiaceae	*Rhus chinensis*	2	1	0	1	1	2	3	2	2
Zingiberaceae	*Alpinia japonica*	0	0	2	0	1	1	0	0	1
Plantaginaceae	*Plantago asiatica*	0	0	1	0	1	0	0	0	1
	P. major	0	0	0	1	0	1	0	1	0
Pteridaceae	*Pteris multifida*	3	2	3	4	2	2	3	4	3
	P. nervosa	3	3	4	2	2	4	2	4	4
Malvaceae	*Hibiscus syriacus*	0	0	0	2	2	1	0	1	3
Aquifoliaceae	*Ilex cornuta*	0	0	3	3	4	3	0	4	3
Pteridiaceae	*Pteridium aquilinum*	3	4	5	5	4	3	2	4	3
Meliaceae	*Melia azedarach*	0	0	1	2	1	0	0	2	3
Papaveraceae	*Macleaya cordata*	0	1	3	4	3	3	2	3	5
Urticaceae	*Boehmeria nivea*	0	0	0	2	0	1	0	0	3
Legum inosae	*Medicago sativa*	0	0	0	0	0	1	0	0	2
	Lespedeza cuneata	0	0	1	1	1	0	0	0	1
Dryopteridaceae	*Dryopteris scottii*	1	1	3	0	2	3	3	2	1

Note [a] Abundance is classified as five grades: 0 means absent; 1 means very rare; 2 means rare; 3 means occasional; 4 means frequent; and 5 means abundant of vegetation community were formed by the activities of radionuclides in and pH value of the uranium tailings. The plant species in the locations of S4, S8, and S9 formed a relatively stable vegetation community (*C. camphora* and *B. papyrifera* + *Loropetalum chinense* and *Vitex negundo* + *Macleaya cordata* and *Phytolacca acinosa*). The plant species in the locations of S3, S5, and S6 formed the transitional vegetation community (*B. papyrifera* + *Mallotus apelta* and *Ilex cornuta* + *M. floxidulus* and *P. aquilinum*). The plant species in the locations of S1, S2, and S7 formed a simple unstable vegetation community (*P. australis* + *I. cylindrica*) and a vegetation community (*M. apelta* + *R. chinensis* + *S. viridis* + *I. cylindrica* + *P. scrobiculatum*) that was similar to that on the unused grassland.

4 Concentration of a Target Radionuclide in the Plant

The most important step to success in phytoremediation is to identify hyperaccumulators which can accumulate a target radionuclide to a certain concentration in their shoots in terms of dry weight. Baker and Brooks (1989) have proposed that the accumulators should have accumulation capabilities of more than 1,000 mg kg^{-1} for As, Pb, Cu, Ni, and Co, 10,000 mg kg^{-1} for Mn and Zn, and 100 mg kg^{-1} for Cd in their shoots. For an accumulator, the metal concentration in its shoot should be much higher than that in its root, and it should have a special capability of absorbing, transferring, and accumulating the metal in its aboveground part (Baker and Brooks 1989). More than 45 families have been identified to contain some metal-accumulating species, and more than 400 plant species of metal hyperaccumulators have been reported (Salt et al. 1998; Reeves and Baker 2000; Hu et al. 2013). But, the hyperaccumulators for radionuclides have not been defined so far. In recent years, phytoremediation studies concerning the treatment of radionuclide-contaminated soils have been carried out using different plant species under various conditions, and the improvement of the uptake by adding fertilizers, organic acids, or chelating agents (Khatir Sam 1995; Papastefanou 1996; Huang et al. 1998; Carini 1999; Madruga et al. 2001; Blanco Rodríguez et al. 2002; Shahandeh and Hossner 2002; Dushenkov 2003; Karunakara et al. 2003; Shinonaga et al. 2005; Soudek et al. 2007a, b, 2010, 2011; Pulhani et al. 2005; Chen et al. 2005; AbdEl-Sabour 2007; Thiry and Van 2008; Vera et al. 2008, 2009; Cukrov et al. 2009; Blanco Rodríguez et al. 2010; Dragović et al. 2010; Srivastava et al. 2010; Černe et al. 2011; Li et al. 2011; Hu et al. 2014). Also, sunflower (*Helianthus annuus*) and Indian mustard (*Brassica juncea*) were proposed as potential uranium accumulators for uranium phytoextraction in one uranium mill tailings soil and nine acid and calcareous soils contaminated with different rates of uranyl nitrate. However, various factors, such as the physical and chemical properties of the soil, water, and sediment, climatic and seasonal conditions, plant and microbial exudates, bioavailability of metals, and the capability of plants to uptake, accumulate, translocate, sequester and detoxify metals, have influence on phytoremediation efficiency (Pedron et al. 2009). As a result, sunflower (*Helianthus annuus*) and Indian mustard (*Brassica juncea*) have not been widely utilized for phytoremediation in practice so far (Fellet et al. 2007). Consequently, it is important to develop phytoremediation technology based on the native plant species that are suitable for the phytoremediation of the sites contaminated by particular radionuclides.

In July 2009, 15 dominant plant species belonging to 9 families were collected from the uranium mill tailings impoundment in South China (Li et al. 2011). The concentrations of uranium and thorium in the samples of plant species and tailings were determined. The results are presented in Table 3. Among the plant samples collected, *Cyperus iria* accumulated the highest concentration of U in its shoot which reached 36.4 μg g^{-1} (Air dried or oven dried weight basis of samples (DW)). *Juncellus serotinus* accumulated the highest concentration of Th in its root which reached 3.66 μg g^{-1} (DW).

In September 2009, a wide survey was conducted in the uranium mill tailings impoundment in South China (Ding et al. 2010). Thirty-five plant species were collected, and the concentrations of uranium in the samples were determined. The results are presented in Table 4. *J. serotinus* accumulated the highest concentration of U in its stem which reached 1.52 mg g^{-1} (Ash weight basis of samples (AW)). Furthermore, *K. brevifolia, C. difformis, M. cordata, Geranium carolinianum, E. annuus, P. nervosa, C. iria,* and *A. fatua* accumulated relatively high concentrations of U in their aerial parts.

In September 2011, an extensive survey was conducted in the uranium mill tailings impoundment in South China (Hu et al. 2014). Thirty-three dominant plant species belonging to 16 families were collected, and the activities of ^{226}Ra in the samples were determined. The results are presented in Table 5. There was great variation in the activities of ^{226}Ra in the tissues of different plant species. The average activities of ^{226}Ra in terms of AW for seeds, leaves, stalks, and roots were 30.99, 13.34, 5.772, and 4.515 Bq g^{-1}, respectively. The high activities of ^{226}Ra were found in the leaves of *P. multifida* (150.6 Bq g^{-1} of AW), in the leaves of *P. aquilinum* (122.2 Bq g^{-1} of AW), in the leaves of *D. scottii* (105.7 Bq g^{-1} of AW), and in the seed of *P. fugax* (105.5 Bq g^{-1} of AW). In contrast, the activity of ^{226}Ra was found below the detection limit in the stalk and root of *Ixeris chinensis* and in the stalk of *S. nigrum*.

Although the hyperaccumulators for U, Th, and ^{226}Ra have not been defined so far, Baker and Brooks (1989) have proposed a two criteria approach for defining the metal hyperaccumulator. First, the concentration of an element accumulated in an organism can be higher than that in the soil. Second, the amount of an element accumulated in an organism can be 10 times greater than that in other organisms investigated. Based on this approach, *C. iria* and *J. serotinus* satisfied the criteria for a hyperaccumulator for U. *P. multifida*, *P. aquilinum*, and *D. scottii* satisfied the criteria for a hyperaccumulator for ^{226}Ra. Although the high concentration of a target radionuclide in the plant species has been found in our investigation, all the experiments were carried out on contaminated areas with different histories, different contents of nutrients and organic matter; the areas were situated in different vegetation climates; and the plant species growing naturally on these areas were also quite different. In the further study, the laboratory tests will be conducted to confirm the results.

Table 3 Concentrations of U and Th in the plant and tailings samples collected from the uranium mill tailings impoundment in South China (DW μg g^{-1}) (Li et al. 2011)

Site	Family	Species	Plant part	U		Th	
				Plant	Tailings	Plant	Tailings
1	Gramineae	*Paspalum paspaloides*	Shoot	8.32	26.7	1.21	4.75
			Root	1.98		0.78	
2	Gramineae	*Miscanthus floridulus*	Leaf	0.96	23.3	0.19	8.84
			Stalk	0.64		0.56	
			Root	1.26		1.20	
	Verbenaceae	*Vitex negundo var . cannabifolia*	Leaf	1.53		0.62	
			Stalk	0.61		0.16	
3	Gramineae	*Paspalum orbiculare*	Shoot	6.99	39.6	2.32	19.8
			Root	1.38		0.23	
	Phytolaccaceae	*Phytolacca acinosa*	Seed	3.55		0.55	
			Stalk	1.40		0.09	
	Compositae	*Artemisia capillaris*	Shoot	0.94		0.29	
4	Euphorbiaceae	*Euphorbia hirta*	Shoot	1.70	21.8	0.26	10.4
			Root	4.98		0.75	
5	Moraceae	*Broussonetia papyrifera*	Leaf	1.54	29.9	0.41	17.8
			Stalk	0.78		0.09	
6	Gramineae	*Phragmites australis*	Seed	1.56	46.5	0.42	10.9
			Leaf	0.36		0.06	
			Stalk	20.6		2.52	
			Root	8.87		1.54	
		Cynodon dactylon	Shoot	1.54		0.25	
7	Cyperaceae	*Kyllinga brevifolia*	Seed	1.09	8.93	0.31	16.6
			Leaf	4.03		2.41	
			Root	7.73		0.53	
8	Cyperaceae	*Cyperus iria*	Shoot	36.4	6.03	2.54	19.2
			Root	2.43		1.54	
9	Cyperaceae	*Juncellus serotinus*	Shoot	16.9	42.1	2.21	8.71
			Root	20.8		3.66	
10	Dicksoniaceae	*Cibotium barometz*	Shoot	5.15	17.3	0.33	18.8
			Root	21.3		1.77	
11	Vitaceae	*Parthenocissus quinquefolia*	Leaf	1.58	26.9	0.04	19.5
			Stalk	0.22		0.57	

5 Biomass of the Plant

The potential of a plant to be used in phytoremediation does not merely depend on the concentration of a target element in the plant (Verma et al. 2007). It has been proposed that a plant with low dry biomass would share a low resultant capability of accumulation for an element and would not be suitable for phytoremediation though the concentration of the target element would be very high in this plant (Robinson et al. 1997). The dry biomass of the plant is considered as an important

Table 4 Concentrations of U in the plant samples collected from the uranium mill tailings impoundment in South China (AW mg g^{-1}) (Ding et al. 2010)

Species	Part	U	Species	Part	U
Imperata cylindrica	Shoot	0.014	*P. nervosa*	Shoot	0.146
	Root	0.077		Root	0.127
Eragrostis pilosa	Shoot	0.057	*Ixeris chinensis*	Shoot	0.016
	Root	0.400		Root	0.032
Kyllinga brevifolia	Shoot	0.124	*Artmsiae capillaris*	Shoot	0.005
	Root	0.084		Root	0.234
C. difformis	Shoot	0.721	*Cyperus iria*	Shoot	0.122
	Root	0.338		Root	0.315
Oxalis violacea	Whole plant	0.048	*Setaria viriisd*	Whole plant	0.304
Common mouse-ear	Whole plant	0.024	*Rhus chinensis*	Leaf	0.242
H. gnaphaii	Whole plant	0.335		Stem	0.205
Macleaya cordata	Leaf	0.111	*Ilex cornuta*	Leaf	0.023
	Stem	0.087		Stem	0.350
Clerodendrum cyrtophyllum	Leaf	0.023	*Helicteres angustifolia*	Leaf	BDL
	Stem	0.048		Stem	BDL
Geranium carolinianum	Leaf	0.444	*Eleusine indica*	Leaf	0.032
	Stem	0.004		Stem	0.111
	Root	0.120		Root	0.050
Paspalum scrobiculatum	Leaf	0.115	*Scirpus planiculmis*	Seed	0.160
	Stem	0.082		Stem	0.004
	Root	0.153		Root	0.033
Heteropogon contortu	Leaf	0.022	*Juncellus serotinus*	Leaf	0.416
	Stem	0.050		Stem	1.520
	Root	0.091		Root	0.345
Pteris multifida	Leaf	0.15	*E. canadensis*	Leaf	0.103
	Stem	BDL		Stem	0.004
	Root	0.361		Root	0.610
Erigeron annuus	Leaf	0.466	*Humulus scandens*	Leaf	0.010
	Stem	0.038		Stem	0.128
	Root	0.012		Root	0.036
Solanum nigrum	Leaf	0.005	*Couch grass*	Leaf	0.028
	Stem	0.043		Stem	0.021
	Root	0.144		Root	0.024
Pteridium aquilinum	Leaf	0.037	*Phleum alpinum*	Flower	0.008
	Vein	0.015		Stem	0.088
	Rhizome	0.053		Root	0.191
Polypogan fugax	Fruit	0.012	*Miscanthus floxidulus*	Fruit	BDL
	Leaf	0.102		Leaf	0.013
	Stem	0.14		Stem	0.014
	Root	0.246		Root	0.025
Phragmites australis	Fruit	0.034	*Avena fatua*	Seed	0.568
	Leaf	0.003		Leaf	0.408
	Stem	0.006		Stem	0.021
	Root	0.074		Root	0.070

Note BDL means below detection limit

Table 5 Activities of ^{226}Ra and TF in the frequently occurred plant species from the uranium mill tailings impoundment in South China (AW ^{226}Ra g Bq^{-1}) (Hu et al. 2014)

Family	Species	Plant tissue	Activity	TF
Moraceae	*Broussonetia papyrifera*	Leaf	4.449 ± 0.256a	0.270
		Stalk	0.065 ± 0.002b	0.004
Oxalidaceae	*O. corymbosa*	Leaf	0.685 ± 0.365c	0.042
		Stalk	0.064 ± 0.026b	0.004
		Root	1.256 ± 0.065d	0.076
Verbenaceae	*Clerodendrum cyrtophyllum*	Leaf	1.660 ± 0.085e	0.101
		Stalk	5.786 ± 0.368f	0.351
		Root	16.31 ± 0.854g	0.989
Cyperaceae	*Kyllinga brevifolia*	Leaf	0.871 ± 0.005c	0.053
		Stalk	3.328 ± 0.152h	0.202
		Root	17.94 ± 0.951g	1.088
	Juncellus serotinus	Leaf	0.536 ± 0.022c	0.032
		Stalk	0.006 ± 0.001j	0.000
		Root	0.805 ± 0.025c	0.049
	Cyperus iria	Leaf	0.015 ± 0.002k	0.001
		Stalk	0.004 ± 0.001j	0.000
		Root	0.019 ± 0.001k	0.001
	Cyperus rotundus	Leaf	0.028 ± 0.002l	0.002
		Stalk	0.015 ± 0.001k	0.001
		Root	1.322 ± 0.095d	0.080
Rosaceae	*R. hanceanus*	Leaf	0.005 ± 0.001j	0.000
		Stalk	0.025 ± 0.001l	0.002
		Root	0.068 ± 0.002b	0.004
Poaceae	*Avena fatua*	Seed	5.190 ± 0.352f	0.315
		Leaf	0.515 ± 0.025c	0.031
		Stalk	6.356 ± 0.423f	0.385
		Root	0.325 ± 0.021c	0.020
	Phragmites australis	Seed	0.421 ± 0.025c	0.026
		Leaf	0.271 ± 0.012c	0.016
		Stalk	0.355 ± 0.015c	0.022
		Root	12.36 ± 0.658m	0.749
	Paspalum scrobiculatum	Leaf	10.37 ± 0.520m	0.629
		Stalk	0.008 ± 0.001j	0.000
		Root	0.569 ± 0.025c	0.034
	Imperata cylindrica	Leaf	3.457 ± 0.080h	0.210
		Stalk	0.007 ± 0.001j	0.000
		Root	0.034 ± 0.002l	0.002
	Eragrostis pilosa	Leaf	0.771 ± 0.008c	0.047
		Stalk	0.468 ± 0.028c	0.028
		Root	0.388 ± 0.015c	0.024
	Eleusine indica	Leaf	5.702 ± 0.210f	0.346
		Stalk	7.513 ± 0.365f	0.455
		Root	5.426 ± 0.151f	0.329

(continued)

Table 5 (continued)

Family	Species	Plant tissue	Activity	TF
	Miscanthus floxidulus	Seed	12.65 ± 0.543m	0.767
		Leaf	0.006 ± 0.001j	0.000
		Stalk	1.367 ± 0.082d	0.083
		Root	16.44 ± 0.752g	0.997
	Phleum alpinum	Leaf	1.539 ± 0.062e	0.093
		Stalk	0.500 ± 0.015c	0.030
		Root	0.647 ± 0.018c	0.039
	Polypogon fugax	Seed	105.5 ± 5.321n	6.408
		Leaf	5.039 ± 0.356f	0.306
		Stalk	0.012 ± 0.001k	0.001
		Root	5.699 ± 0.251f	0.346
	Setaria viridis	Leaf	1.340 ± 0.120d	0.081
		Stalk	0.853 ± 0.025c	0.052
		Root	0.682 ± 0.031c	0.041
Asteraceae	*Artmsiae capillaris*	Leaf	0.423 ± 0.023c	0.026
		Stalk	4.494 ± 0.215a	0.272
		Root	21.021 ± 0.541o	1.274
	Erigeron annuus	Leaf	0.025 ± 0.001l	0.002
		Stalk	0.036 ± 0.002l	0.002
		Root	0.045 ± 0.002l	0.003
	E. canadensis	Leaf	2.086 ± 0.121p	0.126
		Stalk	13.55 ± 0.523m	0.822
		Root	7.197 ± 0.251f	0.436
	H. gnaphaii	Leaf	0.956 ± 0.041c	0.058
		Stalk	0.569 ± 0.021c	0.034
		Root	3.271 ± 0.158h	0.198
	Ixeris chinensis	Leaf	0.069 ± 0.005b	0.004
		Stalk	BDL	–
		Root	BDL	–
Solanaceae	*Solanum nigrum*	Leaf	0.182 ± 0.011q	0.011
		Stalk	BDL	–
		Root	0.682 ± 0.021c	0.041
Ulmaceae	*Trema dielsian*	Leaf	3.612 ± 0.245h	0.219
		Stalk	0.081 ± 0.005b	0.005
		Root	1.368 ± 0.052d	0.083
Euphorbiaceae	*Mallotus apelta*	Leaf	0.052 ± 0.004b	0.003
		Stalk	0.125 ± 0.011q	0.008
		Root	0.068 ± 0.008b	0.004
Anacardiaceae	*Rhus chinensis*	Leaf	0.278 ± 0.015c	0.017
		Stalk	8.106 ± 0.561f	0.491
Pteridaceae	*Pteris multifida*	Leaf	150.6 ± 7.65r	9.131
		Stalk	53.65 ± 2.98s	3.251
		Root	1.782 ± 0.092e	0.108
	P. nervosa	Leaf	14.02 ± 0.820m	0.850
		Stalk	2.354 ± 0.105p	0.143
		Root	0.627 ± 0.052c	0.038

(continued)

Table 5 (continued)

Family	Species	Plant tissue	Activity	TF
Aquifoliaceae	*Ilex cornuta*	Leaf	0.702 ± 0.055c	0.043
		Stalk	3.477 ± 0.254h	0.211
Pteridiaceae	*Pteridium aquilinum*	Leaf	122.2 ± 4.325t	7.409
		Stalk	42.36 ± 1.428u	2.568
		Root	13.14 ± 0.522m	0.797
Papaveraceae	*Macleaya cordata*	Leaf	2.100 ± 0.120p	0.127
		Stalk	5.283 ± 0.428f	0.320
		Root	0.248 ± 0.020c	0.015
Dryopteridaceae	*Dryopteris scottii*	Leaf	105.7 ± 6.650n	6.408
		Stalk	29.685 ± 1.050v	1.800
		Root	5.699 ± 0.467f	0.346

Note Data are presented as mean ±SD, $n = 6$. Means of the data within the column with the same letter are not of significant difference ($p < 0.05$)

factor. The removal capability of a plant for a target element in the plant samples collected was assessed by multiplying the concentration of the target element with the dry biomass of the plant. The average biomass (g) and the removal capability for U and Th (μg plant^{-1}) of the plants collected from the uranium mill tailings impoundment in South China are shown in Table 6. *P. australis* had the greatest removal capabilities for U and Th, which could remove 820 μg U and 103 μg Th per plant, respectively.

6 Concentration of a Target Radionuclide in the Radioactive Waste

The concentration of a target element in the tailings is another important factor that determines the duration it takes to complete the phytoremediation. Phytoremediation might be best suited for sites with the levels of radionuclide contamination which are only slightly higher than the cleanup target levels because the resulting amount of time for cleanup becomes reasonable (less than 10 years) and because possible plant toxicity effects are avoided (Schnoor 2002).

The concentrations of U, Th, and ^{226}Ra in the tailings samples collected from the uranium mill tailings impoundment in South China are presented in Table 1. The concentrations of U ranged from 6.03 to 46.5 μg g^{-1}, Th ranged from 4.75 to 19.8 μg g^{-1}, and ^{226}Ra ranged from 7.32 to 29.52 Bq g^{-1} of DW in the uranium mill tailings. The concentrations of U, Th, and ^{226}Ra in the tailings varied greatly with the sampling sites. This was probably caused by the pH value of the tailings in the sampling sites, microbial community composition and its metabolism, and the plant species growing on them (Li et al. 2011; Hu et al. 2014). The minimum and maximum concentrations of U in the tailings exceeded the background concentrations of U in the soil in the impoundment located in Hunan Province by 1.46

Table 6 Average biomass (g) and the removal capability for U and Th (μg plant^{-1}) of the plants collected from the uranium mill tailings impoundment in South China (Li et al. 2011)

Species	Plant part	Biomassing	Removal capability (μg plant^{-1})	
			U	Th
Paspalum paspaloides	Shoot	1.90 ± 0.15	16.6 ± 1.37	2.61 ± 0.23
	Root	0.40 ± 0.06		
Miscanthus floridulus	Leaf	53.50 ± 6.25	102 ± 15.9	56.3 ± 10.2
	Stalk	49.80 ± 8.24		
	Root	15.20 ± 3.63		
Vitex negundo var. cannabifolia	Leaf	16.20 ± 1.32	38.0 ± 4.25	13.5 ± 1.40
	Stalk	21.60 ± 3.65		
Paspalum orbiculare	Shoot	2.40 ± 0.56	17.6 ± 3.96	5.71 ± 1.31
	Root	0.60 ± 0.03		
Phytolacca acinosa	Seed	2.70 ± 0.03	43.6 ± 3.16	3.68 ± 0.21
	Stalk	24.30 ± 2.18		
Artemisia capillaris	Shoot	17.80 ± 1.95	16.7 ± 1.83	5.16 ± 0.57
Euphorbia hirta	Shoot	5.60 ± 0.46	13.5 ± 1.08	2.06 ± 0.16
	Root	0.80 ± 0.06		
Broussonetia papyrifera	Leaf	18.80 ± 2.36	51.2 ± 6.45	10.3 ± 1.29
	Stalk	28.50 ± 3.61		
Phragmites australis	Seed	1.28 ± 0.05	820 ± 114	103 ± 14.1
	Leaf	13.60 ± 1.65		
	Stalk	37.00 ± 5.32		
	Root	5.62 ± 0.36		
Cynodon dactylon	Shoot	0.68 ± 0.02	1.05 ± 0.03	0.17 ± 0.01
Kyllinga brevifolia	Seed	0.22 ± 0.01	7.18 ± 0.89	3.32 ± 0.49
	Leaf	1.30 ± 0.20		
	Root	0.22 ± 0.01		
Cyperus iria	Shoot	1.26 ± 0.13	46.2 ± 4.76	3.42 ± 0.35
	Root	0.14 ± 0.01		
Juncellus serotinus	Shoot	1.42 ± 0.13	28.8 ± 2.62	3.98 ± 0.36
	Root	0.23 ± 0.02		
Cibotium barometz	Shoot	3.64 ± 0.26	37.1 ± 2.62	2.72 ± 0.19
	Root	0.86 ± 0.06		
Parthenocissus quinquefolia	Leaf	18.50 ± 2.19	30.5 ± 3.60	3.93 ± 0.45
	Stalk	5.60 ± 0.64		

and 17.6 times, respectively. When compared to the background concentrations of U in the soil around the world, the minimum and maximum concentrations of U exceeded by 3.01 and 22.80 times, respectively (Nie et al. 2010). The maximum concentrations of Th in the tailings exceeded the background concentrations of Th in the soil in China by 1.55 times. When compared to the background concentrations of U in the soil around the world, the maximum concentrations of Th exceeded by 2.20 times (Nie et al. 2010). The minimum and maximum activities of ^{226}Ra in the tailings exceeded the background activity of ^{226}Ra in the soil in the impoundment located in Hunan Province by 6,150 and 1,525 times, respectively

(Pan and Yang 1988; Li and Zheng 1989). When compared to the background activity of ^{226}Ra in the soil around the world, the minimum and maximum activities of ^{226}Ra exceeded by 9,973 and 2,473 times, respectively (Bowen 1979). The high concentrations of U, Th, and ^{226}Ra in the tailings made the impoundment a potentially hazardous radioactive source to the plants and animals in and around it. It needs to be remediated urgently.

7 Transfer Factor

Baker and Brooks (1989) proposed that the metal hyperaccumulator should satisfy a criterion that the concentration of an element accumulated in an organism can be higher than that in the soil. Based on their definition, the transfer factor (TF) can be defined as the ratio of target element concentration in the plant to that in the tailings, and it can be used as an index for the accumulation of a target element in the plant and its transfer from the tailings to the plant. If TF for a plant is larger than 1 and the amount of the target element accumulated in the plant is relatively small, the removal capability of the plant for the target element can be further improved using various breeding techniques, and it can be used for phytoremediation (Whicker et al. 1999).

The TFs for U and Th of the plants collected from the uranium mill tailings impoundment in South China are presented in Table 7. *C. iria* had a higher TF for U (5.48), compared with the collected plant species and the reported accumulation plants for U (Shahandeh and Hossner 2002; Chen et al. 2005). But the relatively small amount of biomass in *C. iria* may be a limiting factor for phytoremediation in this study (Table 6). TFs for U and Th of the other plant species were lower than one. TF for ^{226}Ra of the plants collected from the uranium mill tailings impoundment in South China is presented in Table 5. The TF for different tissues of the plant species ranged from 0.000 (leaf of *R. hanceanus* and *M. floxidulus*; stalk of *J. serotinus*, *C. iria*, *P. scrobiculatum*, *I. cylindrica*, *I. chinensis*, and *S. nigrum*; root of *I. chinensis*) to 9.131 (leaf of *P. multifida*). Different TF values for the plants tissues may be resulted in part from metabolic rate differences between plant species and cultivations (Chen et al. 2005). The factors such as the concentration of a radionuclide, speciation, pH of the tailings, the plant age, and ecotype may modify the uptake and ratio of the content of the element in the plant shoot to that in the plant root (Florijn et al. 1993; Jiang and Singh 1994; Tu et al. 2002). About 91 tissues of plant species had the TF values of less than 1, only 9 tissues of plant species had the TF values of more than 1. Overall, it was found that most of the plant species investigated had low capabilities of transferring U, Th, and ^{226}Ra from the tailings to the plant tissues. The results were agreeable with the previous research results (Pulhani et al. 2005; Chen et al. 2005; Baeza and Guillén 2006; Soudek et al. 2007a, b, 2010, 2011; Lauria et al. 2009; Vera et al. 2009).

Table 7 Transfer factor (*TF*) and phytoremediation factor (*PF*) for U and Th of the plants collected from the uranium mill tailings impoundment in South China (Li et al. 2011)

Species	TF		PF	
	U	Th	U	Th
Paspalum paspaloides	0.27	0.24	0.59	0.48
Miscanthus floridulus	0.04	0.05	3.58	4.30
Vitex negundo var. cannabifolia	0.04	0.04	1.63	1.53
Paspalum orbiculare	0.15	0.10	0.42	0.28
Phytolacca acinosa	0.04	0.01	1.10	0.19
Artemisia capillaris	0.02	0.01	0.42	0.26
Euphorbia hirta	0.10	0.03	0.44	0.14
Broussonetia papyrifera	0.04	0.01	1.71	0.58
Phragmites australis	0.31	0.16	16.6	8.68
Cynodon dactylon	0.03	0.02	0.02	0.02
Kyllinga brevifolia	0.46	0.11	0.61	0.19
Cyperus iria	5.48	0.13	7.61	0.17
Juncellus serotinus	0.41	0.28	0.57	0.36
Cibotium barometz	0.48	0.03	1.08	0.06
Parthenocissus quinquefolia	0.05	0.01	1.13	0.20

8 Phytoremediation Factor

In sum, phytoremediation of target radionuclides from the tailings mainly depends on three parameters including the target radionuclide concentration in the plant, the plant biomass, and the target radionuclide concentration in the tailings. In order to assess the potential of a plant for phytoremediation more comprehensively, a novel coefficient was proposed and termed as PF (Li et al. 2011). This factor is the ratio of the total amount of a target radionuclide accumulated in the plant shoot to the concentration in the tailings at the site where the plant grows. The calculation formula for PF is defined as follows:

$$\mathrm{PF} = \frac{\text{Target radionuclide concentration in the plant shoot} \times \text{biomass of the plant shoot}}{\text{Target radionuclide concentration in the tailings}}$$

In this formula, the shoot refers to the tissue above ground of the plant including the seed, leaf, and stalk. The PF can be used as an index for the capability of a plant to remove the target element from the tailings.

The PFs for U and Th of the plants collected from the uranium mill tailings impoundment in South China are calculated and presented in Table 7. As shown in the Table 7, *P. australis* had the highest PF for U (16.6) and Th (8.68), and it also had the greatest removal capabilities for U (820 μg plant^{-1}) and Th (103 μg plant^{-1}) (see Table 6), compared with other plants collected. The results indicated that PF was agreeable with the plant removal capability. PF extends the conventional definition of hyperaccumulator, and it can easily be obtained. Although the concentration of a target radionuclide in a plant does not satisfy the criteria for a hyperaccumulator, the plant may also be considered as the candidate for phytoremediation if it has relatively high biomass. Based on the PF, *P. australis* and *M. cordata* were selected as the candidates for phytoremediation of uranium-contaminated soils (Li et al. 2011; Ding et al. 2011). *Azolla imbircata* was selected as the candidate for phytoremediation of uranium-contaminated water (Ding et al. 2012a; Hu et al. 2012). *P. australis* was selected as the candidate for phytoremediation of thorium-contaminated soils (Li et al. 2011). *P. multifida* was selected as the candidate for phytoremediation of ^{226}Ra-contaminated soils (Ding et al. 2012b; Hu et al. 2014). Although PF provides a novel reference for identification of a plant capable of remediating the tailings and soils contaminated by the radioactive nuclides and heavy metals on a large scale, the plant biomass at a unit area of land is not considered in this factor. It is necessary that further studies should be performed to improve this factor.

9 Conclusion

To screen the suitable plant species for phytoremediation of radioactive waste, the factors, including the characteristics of radioactive waste, the vegetation plant species and vegetation community composition in the radioactive waste deposited area, the concentration of a target radionuclide in the plant, the biomass of the plant, and the concentration of a target radionuclide in the radioactive waste, were analyzed systematically. The PF, which takes into consideration the concentration of a target element in a plant, the plant shoot biomass, and the concentration of the target element in the tailings or soil surrounding the root of the plant, was proposed for the first time to indicate the removal capability of the plant for the target element from the radioactive waste. Using the PF as the criteria, *P. australis*, *M. cordata,* and *Azolla imbircata* were selected as the candidates for phytoremediation of uranium-contaminated soil, *P. australis* was selected as the candidate for phytoremediation of thorium-contaminated soil, and *P. multifida* was selected as the candidate for phytoremediation of ^{226}Ra-contaminated soil.

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Radionuclide Uptake from Soil to Plants: Influence of Soil Classification

Abdus Sattar Mollah

Abstract The entry of trace contaminants, which are present in the terrestrial environment, into human food chains is controlled in the long term by their uptake by plant roots. The radionuclides released into the environment can give rise to human exposure by the transport through the atmosphere, through aquatic systems, or through soil subcompartments. Soil-to-plant factor is one of the important parameters to be used in transfer models for predicting the concentration of radionuclides in crops/plants and for estimating dose impacts to man. Existing databases are limited to experimental values in a restricted number of soil systems and are largely comprised of temperate environment data. In general, transfer factors show a large degree of variation dependent upon several factors such as soil type, species of plants, and other environmental conditions. Soil-to-plant transfers of the radionuclides varied considerably with the times of deposition also. In general, the variations with the deposition times were by a factor of up to 10. This chapter describes a review of published data on the transfer factor (TF) and classification of soils based on TFs.

Keywords Man-made/natural radionuclides · Soil · Plants · Root uptake · Soil-to-plant transfer factor · Time

Contents

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1 Introduction

Radionuclides exist in the environment either naturally or artificially. The natural and artificial radionuclides that are present in the environment are the main sources of radiation exposure for human beings (UNSCEAR 2000). It has been estimated that on average, 79 % of the radiation to which humans are exposed is from natural sources, 19 % from medical application, and the remaining 2 % from fallout of weapons testing and the nuclear power industry (UNSCEAR 2000). However, most of the public concern over radiation from radionuclides has been due to the global fallout from atmospheric nuclear weapons testing and the operation of nuclear facilities. Both of these activities have introduced a substantial amount of man-made radionuclides into the environment and have caused radionuclide contamination of large areas of land worldwide. The natural radioactive background originates from uranium and thorium series, from potassium-40, and from the interaction of cosmic radiation with matter, while man-made sources include various applications of radionuclides in medicine, industries, consumer products, and nuclear weapons tests. Weathering of the earth's crust is the ultimate mechanism for the release of primordial radionuclides into the soil, which constitutes the principal source of natural background radiation. The principal natural chains are those originating, respectively, from ^{232}Th, ^{238}U, and ^{235}U. ^{232}Th is one of the natural thorium isotopes (together with, e.g., ^{231}Th and ^{234}Th that are, respectively, daughters of ^{235}U and ^{238}U) with a half-life of 1.4 × 1010 years. The final stable product of its decay chain is ^{208}Pb. Thorium is present at different concentrations in the earth crust. The most abundant in the earth crust is ^{238}U followed by a very weak presence of ^{235}U and ^{234}U (Mortvedt 1994). Uranium is found in almost all soils and rocks at different concentrations, depending on the nature and typology of soil (Blanco Rodriguez et al. 2006; Baeza et al. 2005). Artificial radioactivity is present in the environment as a consequence of different anthropogenic sources.

It is possible to enlist some of these, ranging from nuclear weapons to radioactive material leaching from nuclear power plants and waste products of general and medical industry. Artificial radioactivity derives from man activity and is generated in different applications, ranging from nuclear installations, nuclear accident, or normal radionuclides applications used in industry, e.g., medical machinery and different kinds of electronic devices. The primary man-made products are ^{90}Sr and ^{137}Cs (Abbazov et al. 1978; Absalom et al. 1999, 2001; Askbrant and Sandalls 1998). Radionuclides of long half-lives, such as ^{90}Sr and ^{137}Cs, are of special importance from the point of human health, since these nuclides can enter the human body via the food chain and increase the radiation burden for many years. The understanding of mechanisms that affect the radionuclide uptake by plant species which grow under field conditions becomes a subject of increasing interest.

Radioactive contamination of the human environment became a reality on July 16, 1945, when the first fission was tested near the town of Alamogordo in New Mexico, USA. However, large-scale production of anthropogenic radionuclides began when the first nuclear reactor started operation in Chicago on December 2, 1942 (Aarkrog 1994). Prior to the release of large quantities of radioactive fission and activation products into the environment during the atmospheric weapons tests 1945–1963, there was limited scientific interest in the environmental radioactivity as the world inventory of artificial radionuclides was very small (Shaw 2007). Atmospheric testing of nuclear weapons was carried out in two main series from 1952 to 1958 and from 1961 to 1962. The USSR, USA, and UK signed the partial atmospheric test ban treaty in 1963, and thereafter, only a limited number of atmospheric tests were carried out by France, China, and India (MacKenzie 2000).

Contamination of soils with typical fission product radionuclides, such as ^{137}Cs and ^{90}Sr, has persisted for far longer than what was originally expected. Radionuclides in soil are taken up by plants, thereby becoming available for further redistribution within food chains. Radionuclides in the environment can, therefore, eventually be passed on to human beings through food chains and so may represent an environmental threat to the health of populations (UNSCEAR 2000). Although atmospheric testing of nuclear bombs has been banned globally, in the foreseeable future, the nuclear power industry will continue to make an increasing contribution to power consumption, a trend which could help to reduce the global warming process due to the consumption of fossil fuel. As accidental and routine releases of radionuclides from the nuclear industry are inevitable and can cause local, regional, and even global environmental contamination, remediation of soils contaminated with radionuclides is becoming an increasingly important aspect of radiological protection.

Artificial radionuclides have entered the human environment as a consequence of atmospheric nuclear weapons tests. Global fallout of fission products in the 1950s and 1960s involved deposition of ^{137}Cs ($t_{1/2\text{phys}}$: 30.17 years), ^{90}Sr (28.5 years), ^{89}Sr (50.5 days), ^{3}H (12.3 years), ^{54}Mn (312 days), ^{65}Zn (244 days), ^{95}Zr (64 days), $^{103/106}$Ru (39.4 days/368 days), ^{129}I (1.6×10^{7} years), and ^{144}Ce (284.8 days). At present, the most important sources are routine releases from nuclear power (NPP) and reprocessing plants, which can include ^{3}H, ^{14}C, ^{60}Co ($t_{1/2\text{phys}}$:

Table 1 Major global radionuclide releases in PBq (10^{10} Bq) (UNSCEAR 2000)

	^{90}Sr	^{137}Cs	$^{239/240}$Pu
Nuclear weapons tests	622 PBq	948 PBq	11 PBq
Chernobyl	10 PBq	85 PBq	0.07 PBq

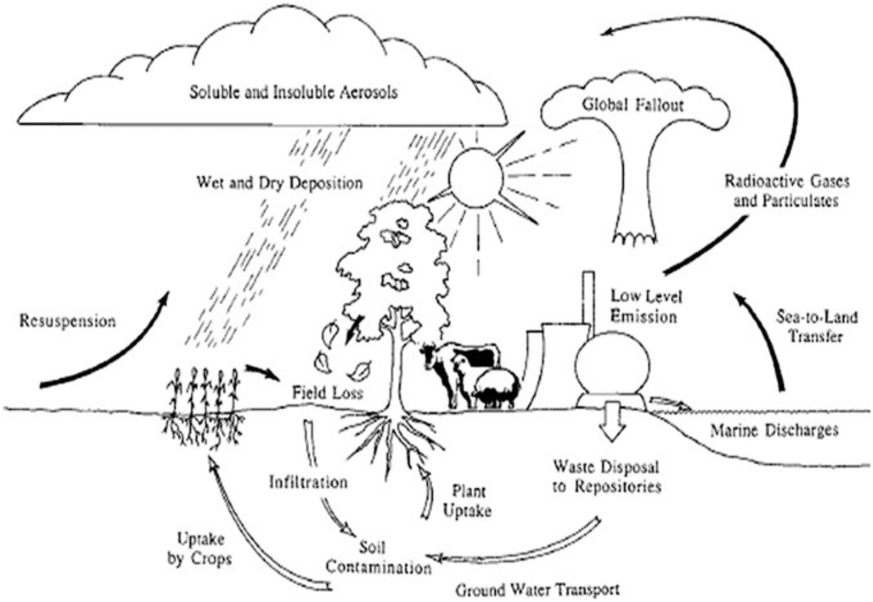


Fig. 1 Pathways leading to redistribution throughout the environment of artificial radionuclides from nuclear-related facilities

5.27 years), ^{54}Mn, ^{89}Sr, ^{90}Sr, ^{95}Zr, ^{85}Kr (10.8 years), ^{238}Pu (87.7 years), $^{239/240}$Pu (24,000 years/6,600 years), ^{129}I, ^{95}Nb (35 days), $^{103/106}$Ru, ^{110m}Ag (249.9 days), ^{125}Sb (2.77 years), $^{134/137}$Cs (2.06 years/30.17 years), ^{140}Ba (12.8 days), and ^{144}Ce (284.8 days).

On a global scale, terrestrial ecosystems have received the largest inputs of anthropogenic radionuclides from nuclear weapons tests and from the accident at the Chernobyl nuclear power plant (UNSCEAR 2000) (Table 1).

Figure 1 illustrates the principal sources of artificial radionuclides released to the environment and the complex pathways by which these sources are redistributed and ultimately impact on organisms. Radionuclides released to the atmosphere and marine waters can be transported over large distances and eventually find their way to the terrestrial environment, often with surprising rapidity. Once terrestrial ecosystems become contaminated through such routes, the residence times and environmental impacts of individual radionuclides within specific ecological compartments is a function of the physical half-life of the radionuclide, the chemistry of the element to which it belongs, and the nature of the compartment itself. Long-lived radionuclides pose environmental hazards on different timescales. Hence, ^{137}Cs and ^{90}Sr (half-lives = 30 and 28 years, respectively) deposited on land surfaces around the world at the peak of atmospheric weapons testing in 1963 are still present in the environment and are likely to remain detectable for another 150 years.

The primary application of soil-to-plant transfer factors is in food chain 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 (Hoffman et al. 1984; Peterson 1995). For this purpose, the use of parameters that are as simple as possible is desirable to keep model complexity down. The wealth of soil-to-plant transfer factor data now available at least for temperate environments seems to be adequate to derive probability distributions from which representative values for use with screening models can be derived (IAEA 1994; Sheppard and Evenden 1997; Nisbet 2000).

In radioecological research, on the other hand, interest shifts more and more to elucidating the chemical, biological, and physical mechanisms governing the root uptake and translocation of radionuclides from soils. The best example may be the pioneering work of Cremers and coworkers (Cremers et al. 1988; Valcke and Cremers 1994) on the chemistry of radiocesium in soils. Recent understanding of processes involved in soil–plant transfer offers the perspective for developing mechanistic models, but such models, although deemed required (Nisbet 2000), are not yet available. Focusing on radiocesium and radiostrontium, this paper intends to summarize present knowledge on processes which influence root uptake of radionuclides (as well as of other trace metals) by plants and to identify areas where our present understanding is still limited. Although important, species variations in soil–plant transfer are not discussed, since comprehensive compilations and reviews are available (e.g., Andersen 1967; Frissel 1992).

Eventually, the most important conceptual limitation of the transfer factor approach is that it does not take into account competition between ions. Soil-to-plant transfer factors are most often measured for trace substances whose behavior in the soil–plant system largely depends on the concentrations of macronutrients present. For example, an activity concentration in a soil solution of 1 Bq l^{-1} of ^{90}Sr or ^{137}Cs corresponds to ca. 2×10^{-15} M l^{-1}, whereas median concentrations of Ca, K, and Mg in soil solution are in the order of 1 mM l^{-1} (Robson and Pitman 1983). A number of substances naturally present in soils have been found to influence the uptake of radionuclides and heavy metals by plants, though not always beneficially (Wallace 1989; Desmet et al. 1991; Lorenz et al. 1994a, b). For radioactive cesium and strontium, these competitive effects form the basis for countermeasures at the soil–plant level after a nuclear accident (Howard and Desmet 1993). As discussed in detail in the following paragraphs, the concentration of a trace substance accumulating in plants may not primarily depend on its absolute concentration in the soil–plant system but on the concentration ratio of other micro- and macronutrients.

In fallout situation, the human population can be exposed to external and internal radiation by different pathways (Fig. 2). As generally found, the transfer to

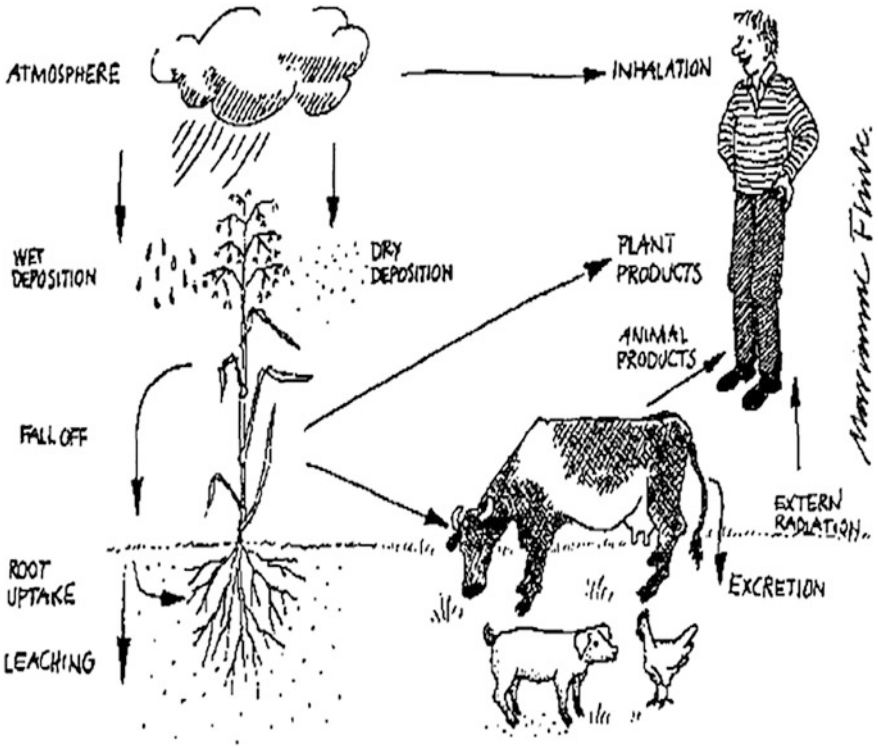


Fig. 2 Main pathways for radionuclides to man

a certain crop will be much less if fallout takes place between two growth seasons than during a growth season. The direct transfer from fallout to a crop exposed to the atmosphere during a growth season will always be much higher than the indirect transfer from a contaminated ground surface, which in turn will be higher than the transfer by root uptake from a contaminated soil or plow layer.

There is increasing interest in radiological assessments of discharges of naturally occurring radionuclides into the terrestrial environment. Such assessments often require the use of predictive models because measurements in environmental materials generally contain a contribution from the natural background. The transfer of artificial radionuclides along terrestrial food chains has been studied extensively over the last 30 years, with understandable emphasis on radiocesium since 1986 (Bunzl and Kracke 1989; Chiu et al. 1999). Naturally occurring radionuclides have not been studied to the same extent as their artificial counterparts, but some comprehensive investigations have been carried out in various parts of the world. There is increasing interest in radiological assessments of the discharges of naturally occurring radionuclides into the terrestrial environment, in terms of current releases both from industrial sites and from the presence of historical contamination in the soil.

The natural and artificial radionuclides that are present in the environment are the main sources of radiation exposure for human beings and constitute the background radiation level (Eisenbud 1973). Contamination of the environment has been a frequent legacy of industrialization, and recognition of the adverse health and environmental and economic effects of this contamination resulted in legislation for its minimization and monitoring. Thus, determining the distribution of these radionuclides is necessary for assessing the effects of radiation exposure (Eisenbud 1973). There is now increasing pressure to develop effective technologies not just to minimize and monitor but to decontaminate ecosystem compartments such as soils that have become contaminated; the nuclear industry is similar to other industries in these respects (Eisenbud 1973).

Radioactivity from the Chernobyl accident affected food production systems throughout Europe. Most affected were the Scandinavian countries where activity concentrations in reindeer, goat's milk, sheep, game animals, and freshwater fish were above the intervention levels, which are still subject to restrictions. Radiocesium and radiostrontium were still present in the global environment at relatively low concentrations prior to the Chernobyl accident as a result of atmospheric nuclear weapons and discharges from natural facilities to a lesser extent. The global fallout of ^{137}Cs resulting from the atmospheric nuclear weapons testing during the 1960s has been estimated at 2.8 kBq^{-1}m^{2} in the Northern Hemisphere and 2.2 kBq^{-1} m^{2} in central Sweden (Rosèn et al. 1999). However, from Chernobyl accident, they were 1.8 and 1.4 kBq^{-1} m^{2}, respectively (Rosèn et al. 1999). The total amount of ^{137}Cs deposited over Sweden has been estimated to be 4.25 × 1015 Bq (UNSCEAR 2000). In some places, the Chernobyl fallout of ^{137}Cs in Sweden was up to 100 times higher than the global bomb fallout (Rosèn et al. 1999). The greater activity of ^{137}Cs in the initial fallout, twice the activity of ^{134}Cs and its longer physical half-life, makes ^{137}Cs the most important of the two cesium isotopes (Rosen et al. 1999).

About 1,300 different radionuclides exist partly originating from natural sources and partly anthropogenically produced. Natural radionuclides can be generated by the activation of stable isotopes via cosmic radiation, for example, ^{3}H (12.3 years of half-life), ^{7}Be (53.3 days), ^{14}C (5,730 years), and ^{35}S (87.5 days) known as cosmogenic radionuclides, which are originated during the creation of the universe. The latter are known as primordial radionuclides and include ^{40}K (1.3 × 109 years) and the isotopes of uranium and thorium that give rise to various daughter nuclides including ^{226}Ra (1,600 years), ^{222}Rn (3.8 days), and ^{210}Pb (22.3 years) (Strebl et al. 2007). Artificial radionuclides have entered the human environment as a consequence of atmospheric nuclear weapons tests and also by nuclear accidents. Global fallout of fission products in the 1950s and 1960s involved deposition of ^{137}Cs (30.17 years), ^{90}Sr (28.5 years), ^{89}Sr (50.5 days), ^{3}H, ^{54}Mn (312 days), ^{65}Zn (244 days), ^{95}Zr (64 days), $^{103/106}$Ru (39.47368 days), ^{129}I (1.6 × 107 years), and ^{144}Ce (284.8 days). At present, the most important sources are routine releases from nuclear power plants (NPP) and reprocessing plants. Very high emissions of these isotopes can occur in very rare circumstances of nuclear power plant accidents such as occurred at Chernobyl (Ukraine) in 1986.

This accident caused deposition of substantial quantities of radionuclides over a large part of Europe, and in Sweden, four counties were mainly affected (Rosén et al. 1999). Hence, it increased the $^{134/137}$Cs and ^{90}Sr soil inventories of Sweden and many other European countries considerably (Strebl et al. 2007). In the USA, many nuclear plant accidents were occurred and caused fatalities and property damages. One of them is the accident happened in Idaho Falls, Idaho, January 3, 1961, where the damage costs around 22 million dollar.

In Japan, the Fukushima I nuclear accidents occurred after a 9.0 magnitude Tōhoku earthquake and subsequent tsunami on March 11, 2011, only 14 days before the reactor was to be shut down. The earthquake triggered a scram shutdown of the three active reactors at the Fukushima I Nuclear Power Plant (Fukushima Dai-Ichi). The ensuing tsunami inundated the site, stopped the Fukushima I backup diesel generators, and caused a station blackout. The subsequent lack of cooling led to explosions and meltdowns at the Fukushima I facility, with problems at three of the six reactors and in one of the six spent fuel pools. It caused fatalities and properties damage and evacuation of millions of people.

Irradiation of humans can occur via external and internal exposure to radionuclides (Voigt et al. 2007). Doses to humans are estimated by considering ingestion of radionuclides in drinking water and food, external irradiation from radionuclides in soil, and inhalation of radionuclides on airborne dust particles, and these accounts for a substantial part of the average radiation doses received by various organs of the human body (Khan et al. 2010; Voigt et al. 2007).

Plants acquire man-made and naturally occurring radionuclides via their roots or leaves, and animals acquire them through consumption of plants, phosphate-based mineral food supplements, and soils. These radionuclides are ultimately transferred to man by eating animal meat or milk or directly from plants by using them as food. Radionuclides ingested in food and, to a lesser extent, water account for a substantial part of the average radiation doses received by various organs of the human body, especially the skeleton. Certainly, radionuclides in an environment will persist with more or less predictable residence times and with associated radiation exposures in proportion to the type and activities of radionuclides present. Radioactivity from the Chernobyl accident affected food production systems throughout Europe.

Plant development stage and seasonality are the varying response to radioactive contamination of vegetation when the contamination occurs. Furthermore, the migration and accumulation of radionuclides in the soil–plant system is a complex phenomenon, involving processes such as leaching, capillary rise, runoff, sorption, root uptake, and resuspension into the atmosphere (Ehlken and Kircher 2002; Frissel et al. 1990; Fortunati et al. 2004; Haylock 1999; Higley and Bytwerk 2007; Kabate-Pendias 2004). The plant uptake of the main natural radionuclides, uranium, thorium, potassium, and radium, is naturally due to the plant's need of nutrients. Through the mineral uptake process, the plant transfers natural radioactive substances, which accumulate in the plant vital portions, including the edible ones. Radionuclides are taken up by plants by some of the same mechanisms (Baeza et al. 2004; Frissel 1990; Duskesas 2009; Bunzl 1997; Bynzl et al. 2000; Choi et al. 1998; Djingova et al. 2005; Djuric et al. 1996; Djingova and Kuleff 2002) as plant nutrients due to their similar chemical and physical characteristics. In this way, radionuclides enter human food chain through consumption and lead to a long-term internal exposure to human body (Pulhani et al. 2005). This chapter describes a review of published data on the transfer factor and classification of soil based on TFs.

2 Transfer Factors

Radionuclide uptake by plants from contaminated soil represents a key step of radionuclide input into human food chain; this phenomenon is described by soil–plant transfer factor that is defined as the ratio of plant-specific activity to soil-specific activity. Plants are the primary recipients of radioactive contamination to the food chain following atmospheric releases of radionuclides. The transfer factor (TF) is a value used in evaluation studies on impact of routine or accidental releases of radionuclide on the environment for most important agricultural products known. For other areas and especially the developing countries, TFs are less known. The soil-to-plant transfer factor is regarded as one of the most important parameters in environmental safety assessment needed for nuclear facilities. This parameter is necessary for environmental transfer models which are useful in the prediction of the radionuclide concentrations in agriculture crops for estimating dose intake by man.

Plants are the primary recipients of radioactive contamination to the food chain from the abiotic environment through the uptake of radioactive debris from the atmosphere by aboveground parts of plants and a sorption of debris from the soil by the root system of plants (Aarkrog 1994). Experience since the Chernobyl accident indicates that the intake of radioactivity through food is an important source of the dose to the population in the Nordic countries such as Sweden. In the long term, the problems will be connected to the contamination of various sensitive ecosystems. Plant development stage and seasonality are the varying response to radioactive contamination of vegetation when the contamination occurs. Short-lived radionuclides (as ^{131}I) and those that enter the food chain by direct contamination (e.g., ^{137}Cs) are important in this connection (Aarkorg 1994).

Radionuclides from natural decay chains despite short physical half-lives can be of high radiological importance because they are continuously produced and thus remain in the environment at a constant level (Streble et al. 2007). Besides the total amount deposited, the radiological importance of artificial radionuclides is determined by their radioactivity and radiation type (alpha, beta, or gamma), their bioavailability, and behavior within the food chain (Streble et al. 2007). Some radioactive isotopes like those of iodine cannot be discriminated from the stable forms and readily enter living systems.

The soil–plant–human is the principal pathway being studied for the transfer of radionuclides to human beings (IAEA 1982, 1994, 1999). Soil-to-plant transfer is one of the major environmental pathways leading to human ingestion of radionuclides. Thus, since the 1950s and 1960s, many efforts have been undertaken to predict and quantify radionuclide root uptake and to implement suitable models in radioecological/radiological models. The transfer factor concept is the simplest model for the quantification and prediction of crop contamination with radionuclides. It is usual to adhere to strict protocols when obtaining data to calculate transfer factors, as originally specified by the International Union of Radioecology (IUR 1989; IAEA 2004, 2006, 2009). The radionuclide concentration in soil is always determined on a dry weight basis down to a depth of 20 cm for all crops except pasture grass (10 cm). When determining radionuclide concentrations in plant material, the edible parts of crops (grain, tubers, fruits, edible leaves, etc.) have been most often investigated although, in the case of grazed and seminatural ecosystems, the vegetative parts of plants which provide nutrition for animals are just as important.

Soil–plant–human is recognized as one of the major pathways for the transfer of radionuclides to human beings. Knowledge, description, and modeling of radionuclide transfer in food chains are one of the key topics in radiation protection and radioecology (Voigt et al. 2007). Although the majority of research to date has focused on the contamination of food products and its prediction, an attempt is made here to draw together the more ecological aspects such as the distribution and fluxes or radionuclides in the different compartments. In response, countermeasures to reduce especially radiocesium, radioiodine, and radiostrontium in animal products have been studied, tested, and implemented, including those for animals living in seminatural environments. However, to apply countermeasures most effectively, the behavior and transfer of radionuclides in animals need to be understood and properly modeled (Voigt et al. 2007).

An important assumption in using the TF is that it is independent from the absolute radionuclide concentration in the soil. This assumption does not always appear to hold true under real-world conditions (Bunzl et al. 2000). Other simplifications in the transfer factor concept include (1) the artificial definition of the rooting zone, (2) the lack of discrimination between radionuclide pools of different availability in soil, (3) the fact that the TF does not really describe the process of root uptake but merely provides a concentration ratio including, for example, mass loading of plant surfaces with contaminated soil particles, and (4) the omission of any plant physiological parameters. The influence of these and additional simplifications discussed above is reflected by the huge variability of transfer factor values obtained under field and experimental conditions, which, for many radionuclides, exceeds three orders of magnitude (Coughtrey et al. 1983; IAEA 1994).

Another comprehensive data set published can be found in Gerzabek et al. (1998). A careful evaluation of the available Cs and Sr transfer data was published by Nisbet et al. (1999) who investigated the effects of aging, pH, organic matter, and exchangeable potassium (or calcium) on the soil-to-plant transfer of Cs and Sr. Post-Chernobyl studies confirmed previous work showing the influence of soil properties (clay mineral content and exchangeable potassium concentration) on radiocesium uptake by the food chain (Smith et al. 2005). Important factors affecting the transfer of radiocesium to crops/plants are the distribution of the root system in the soil profile as well as the soil pH and nutrient status (Rosén et al. 1999).

Primordial radionuclides (^{238}U, ^{235}U, ^{232}Th, and ^{40}K) were formed by the same stellar processes which formed the other heavy elements of the earth (Eisenbud 1973). They are long-lived species that have been present on the earth since its formation 4.5×10^9 years ago (MacKenzie 2000). The radionuclides ^{238}U, ^{232}Th, and their decay products and ^{40}K are natural terrestrial radionuclides and significantly form the major part of the natural radiation dose (UNSCEAR 2000). Due to its low natural abundance, ^{235}U and its decay products do not form a significant part of natural radiation exposure. The primordial radionuclides ^{238}U, ^{235}U, and ^{232}Th are the parent members of the three natural radioactive decay series, and their main members along their half-lives and principal decay modes are shown below (MacKenzie 2000): Radiation doses from primordial radionuclides are primarily from external gamma radiation, ingesting, and inhalation. Both external and internal doses can vary significantly according to differences in the geology of a region.

The soil-to-plant transfer factor (TF), the ratio of the concentration of radioactivity in the crop to the radioactivity per unit mass (sometimes surface area is used) of the soil, is a value used in evaluation studies on the impact of releases of radionuclides on the environment. The calculated dry weight radioactivity values in the soil and plant samples were used to derive transfer factors from each of the soils into each crop. The definition of a transfer factor is given by the following equation (IAEA 2004):

$$\mathrm{TF} = \frac{\text{Concentration of radionuclide in plant}\left(\mathrm{Bq\,kg^{-1}}\ \text{dry crop mass}\right)}{\text{Concentration of radionuclide in soil}\left(\mathrm{Bq\,kg^{-1}}\ \text{dry soil mass in upper 20 cm}\right)}$$

For grass, the soil depth considered is 10 cm.

Radioactivity in soil is defined here as the average activity concentration in the top 20 cm. This is an accepted international compromise arising from alternate measures that are often based on deposition per unit area assuming atmospheric fallout. Transfer factor values in excess of one imply active bioaccumulation of activity. Values less than one imply either strong binding of the radioactivity to the soil or that the plant is not accumulating that material. For most of Europe and the USA, the TFs for most important agricultural products are known. For other areas and especially the developing countries, TFs are not so readily available (IAEA 1994, 2010).

The transfer factor (TF) is a value used in evaluation studies on the impact of routine or accidental releases of radionuclide on the environment. This parameter is necessary for environmental transfer models that are useful in the prediction of the radionuclide concentrations in agricultural crops for estimating dose intake by man. The main factors that determine the variability of TFs are the type of radionuclide, type of crop, type of soil (soil characteristics), and stable element concentration. Minor factors are differences in crop varieties, differences in agricultural management (fertilization), and differences in the weather. The term weather is used deliberately, because what is meant is not the overall climate but the day-to-day differences of the weather which are believed to be the main reason for the great spread of TFs. As the transfer factors can differ between areas due to different climates, soil types, and vegetation, local transfer factors should be observed.

The transfer of artificial radionuclides along terrestrial food chains has been studied extensively over the last 30 years, with understandable emphasis on radiocesium since 1986. Naturally occurring radionuclides have not been studied to the same extent as their artificial counterparts, but some comprehensive investigations have been carried out in various parts of the world. Many studies have been carried out to determine TFs for most important agricultural products (Nisbet and Woodman 2000; Ng et al. 1982; Muck 1997; Masconzoni 1989; Martinez-Aguirre 1996; Livens et al. 1991; IUR 1992; Jacobson and Overstreet 1998; Deb et al. 2004; Frissel et al. 1990, 2002; Pulhani et al. 2005; Popplewell et al. 1984; Pietrazak-flis and Suplinska 1995; Mollah et al. 1998, 2004; Mollah and Begum 2001). Several projects were run by the International Atomic Energy Agency (IAEA) to determine TF mainly for ^{90}Sr and ^{137}Cs (IAEA 2010). These data have been used extensively in radiological assessment models. Natural environmental radioactivity arises mainly from primordial radionuclides, such as ^{40}K, and the radionuclides from ^{232}Th and ^{238}U series, and their decay products are considered to be the main contributor to internal radiation dose. Several studies on transfer of natural radionuclides from soil to plant have been carried out in different regions in the world (Shappard and Evenden 1988, 1990; Vera Tome et al. 2003; Hanlon 1994; Vandenhove et al. 2009; Yunoki et al. 1993; Yamamoto et al. 1996). However, there seem to be few data on transfer of natural radionuclides from soil to plant in semiarid environments. Therefore, the present study aimed to determine TF for natural radionuclides in semiarid settings to some agricultural crops under natural field conditions.

Transfer factor depends upon many factors such as electrical conductivity (EC), PH, and bicarbonate contents of soil. Radionuclide plant–soil ratio is affected by many factors that control plant uptake. These factors are as follows:

1. Physicochemical form of radionuclide.
2. Plant species and internal translocation mechanisms within the plant.
3. Soil characteristics.
4. Fertilizers and agricultural chemicals.
5. Chelating agents.
6. Distribution of radionuclides in soil.

The physicochemical form of the radionuclide strongly affects its retention by the soil particles and its availability for uptake by plants. The soil type affects strongly the behavior of radionuclides in soil and soil retention characteristics (Skarlou et al. 1996; Remeikis et al. 1957; Riise et al. 1990; Abbazov et al. 1978; Baeza and

Gullen 2006; Champlin and Eichholz 1967). Sandy soils do not have the retention capacity of clay soils. Clay soils are composed of smaller particle sizes with larger surface area and negative charge surfaces. The soil's pH value affects the plants uptake. In alkaline soils (high pH), insoluble precipitates may be formed with carbonate, hydroxyl, phosphate, or sulfide ions. These insoluble precipitates reduce the availability of radionuclides for plants. In acid soils (low pH), hydrogen replaces the adsorbed cations which become more available to plants. In highly acidic soils ($pH < 5.5$), some trace elements (particularly iron and manganese) may become toxic to plant growth. Fertilizers are chemical compounds added to increase the soil fertility and enhance plant production. They strongly affect both the stable element concentration and soil acidity (Fort 1978; Jang et al. 2004; Juo and Barber 1970; Kuhn et al. 1984; Massas et al. 2002). The effect of limestone ($CaCO_3$) addition appears to raise soil pH, increase exchangeable calcium concentration, and decrease the uptake of strontium. This is possibly due to the decreased solubility of $SrCO_3$ in alkaline conditions. Fertilizer with nitrogen in the nitrate form (potassium or calcium nitrates) and phosphate fertilizers may decrease soil acidity (Foth 1978). Organic fertilizer affects the ion exchange capacity, pH, stable element content of soil, and soil retention properties (Champlin and Eichholz 1967; Routson and Cataldo 1978).

Chelating agents are organic compounds which increase the ion mobility and reduce soil retention. This increases the plant uptake. Moreover, these agents enhance the translocation ability within the plant itself (Champlin and Eichholz 1967). In some situations of plant nutrient deficiencies, they are useful because they decrease soil retention, therefore increasing plant uptake (Pickering et al. 1966). Their effectiveness depends upon soil properties (particularly soil pH), chemical form of the radionuclide, and the nature and concentration of chelating agent.

Radiological assessments are always based on a prediction (or reconstruction) of radionuclide transport patterns. Recently, a number of high-quality publications have been produced for many of the transfer parameter values which merit consideration. The primary application of soil-to-plant transfer factors is in food chain 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. For this purpose, the use of parameters that are as simple as possible is desirable to keep model complexity down. The wealth of soil-to-plant transfer factor data now available at least for temperate environments seems to be adequate to derive probability distributions from which representative values for use with screening models can be derived (IAEA 1994; Nisbet and Woodman 2000).

For many years, the IAEA has been publishing documents aimed at the support of the assessment of the radiation impacts on both human beings and the environment. Two major supporting data documents are the Technical Report Series No. 247 (TRS 247) "Sediment K_ds and Concentration Factors for Radionuclides in the Marine Environment" and TRS No. 364 "Handbook of parameter values for the prediction of radionuclide transfer in temperate environments" (IAEA 1994).

The main goal of the Technical Report Series No. 364 “Handbook of parameter values for the prediction of radionuclide transfer in temperate environments” was to provide realistic transfer parameters for radiological assessments. Together, these documents covered available by that time transfer parameters for marine, freshwater, and terrestrial environments, and over many years, they have been key references for assessors, providing environmental impact assessments. In 2000, the IAEA initiated a revision of TRS 247 resulted in the publication of Technical Report Series No. 422 “Sediment Distribution Coefficient and Concentration Factors for Biota in the Marine Environment” (IAEA 2004). However, TRS 422 has proved to be one of the most important sources of information used in assessing the impact of radionuclides on the marine environment and can be widely used for the further development of generic model for to assess the impact of radioactive discharges on marine ecosystems. The document contains revised sediment *Kd*s for marine ecosystems and concentration factor (CF) values for some marine biota species. In addition, TRS 422 contains CFs for a limited number of elements for marine mammals not included in TRS 247. In 2003, in the framework of the IAEA EMRAS (“Environmental Modelling for Radiation Safety”) project, the IAEA also started a revision of TRS 364. The developments of the above documents were supported by several CRPs, namely “Radionuclide Transfer from Air, Soil, and Fresh Water to the Food chain of Man in Tropical and Subtropical Environments,” “The classification of soil systems on the basis of transfer factors of radionuclides from soil to reference plants,” and “Radiochemical, chemical and physical characterization of radioactive particles in the environment” (IAEA 2006).

Investigations on the factors influencing the TF of radiocesium have been reported in an enormous number of studies, especially after the Chernobyl accident. Many of the results have been summarized in Frissel (1992), IAEA (1994), and IUR (1992), Nisbet et al. (1999). From this experimental material, many conclusions have been reached about the influence of some soil, climatic, and agricultural factors on the TF of radiocesium. However, a lot of contradictory facts have accumulated as well, indicating that more needs to be known about the dependence of TF on all soil properties and their combinations and on the regional conditions and seasonal changes which might cause variation in the TF. Therefore, in spite of the numerous existing data during the last decade, the FAO/IAEA initiated two successive coordinated research programs (“Radionuclide transfer from air, soil and freshwater to the food chain of man in tropical and subtropical environments” and “Classification of soil systems on the basis of transfer factors of radionuclides from soils to reference plants”) aiming to propose a classification of soils on the basis of reference values for the transfer of radiocesium and radiostrontium. The preliminary results are reported in Frissel et al. (2002) and Skarlou et al. (2003).

3 Factors Influencing Transfer Factors

The TF values of artificial and natural radionuclides vary enormously. The main factors that cause this variability for any particular radionuclide are the type of crop and type of soil. The length of time the radionuclide has been in the soil is also important. Other factors are crop variety, agricultural practice (especially fertilization), and differences in the weather during the growing season (Fig. 3).

Soil properties that are likely to affect TF values include mineralogical and granulometric composition, organic matter content pH, and fertility. For cations such as Cs^+ and Sr^{2+}, cation exchange capacity and the nature of exchangeable bases are important.

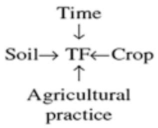
The TF for Cs depends not only on the soil properties but also on the time that the radionuclide has been present in the soil as the availability of Cs decreases with time. A variety of processes are involved including fixation with soil minerals, incorporation by microorganisms, and migration within the rooting zone. Consequently, a reference value is contact time dependent. The TF for Cs in non-equilibrium conditions may be up to a factor 10 higher than for equilibrium conditions. Equilibrium for Cs may take some 5 years to attain, sometimes longer although the rate of decrease in TF is greatest during the first three months. The availability of Sr also decreases with time, but the effect is much less pronounced than with Cs.

Aside from the inherent characteristics of a crop to take up cations, TFs are a function of the physiological state of the plant which is affected by soil fertility (hence agricultural practice), the weather, and its stage of development. In the IAEA CRP (Frisel et al. 2002), this variability is reduced by considering only the radionuclide content of the harvested part of the plant, although for crops such as grass or chard, which are cut several times a season, the TF remains a function of the stage of physiological development.

Soil parameters that exert a major impact on radionuclide mobility are, according to Bunzl (1997), (1) the composition of the soil solution (pH, concentration of inorganic ions, redox potential, and concentration of organic substances), (2) physical and chemical soil properties (species/characteristics and contents of clay minerals, oxides and organic matter, and surface and charges of particles), (3) microorganisms and fungi (mycorrhiza), and (4) temperature. Most radionuclides in soil are present in cationic forms. In general, therefore, low pH values, low clay contents, and low cation exchange capacities lead to an increase in radionuclide mobility within the soil profile and favor plant uptake of radionuclides. Changes in soil organic matter content can yield different effects, depending on the ability of the respective radionuclide to form organic complexes or not (Frissel et al. 1990).

For radionuclides present in terrestrial ecosystem, information about their migration in soils is crucial, since this process controls their long-term behavior in the environment and their uptake by flora and fauna including food chains, but also their potential as groundwater contaminant (MacKenzie 2000). In soil, the type of radionuclide element determines only their potential ability to migrate through the

Fig. 3 Factors affecting TF values



profile. In soil profile, it is believed that the initial movement of deposited radioactive elements or radionuclides from the soil surface is relatively rapid as a result of infiltration process. And, the radionuclide migration intensity is observed as a result of simultaneously occurring processes: transport caused by rainfall infiltration (convective transport), dispersion caused by spatial variations of convective velocities, transfer on colloidal and fine-dispersed particles (diffusion process), migration along the plant root system, and others. In addition to these abiotic processes, soil fauna may contribute to the transport of radionuclides in soils, but their action under general conditions results in a dispersion-like translocation. Hence, the vertical migration of the radionuclides is much slower as a significant amount of the fallout of the majority is sorbed to the soil matrix. However, for some radionuclides such as radiocesium, their mobility might be decreasing over period of time after fallout due to the presence of slow sorption reactions in soil. Thus, the physical and chemical behaviors of the fallout (radionuclides) influence its migration in the soil. The concentration (amount) and distribution of radioactive elements in the root zone of plants also affects the transfer of radioactivity to the food chain and the transport of radioactive elements from contaminated soil to plants (Eisenbud 1973).The factors that determine the variation of radionuclide activity with depth in soil profile are rainfall intensity, pH, organic matter content, soil moisture content, soil texture, soil structure, infiltration rate, sorption characteristics of the particular radionuclide, land use, and management practices (Rosen et al. 1999). Due to the inherent complexity and spatial variability of the soil–plant system, the uptake of radionuclides in vegetation from soil is difficult to quantify. The transfer factor (TF) is a useful parameter, which is usually used for evaluating the impact of releases of radionuclides on the environment (IAEA 1994). The TF depends on the vegetation type, soil properties, and the type of radionuclides (Eisenbud 1973). For example, Velasco (2008) established an association of transfer factors of radiocesium and radiostrontium with soil organic matter, an association which was absent in the data analyzed by Nisbet and Woodman (2000). The enormous number of observations that have been accumulated during the last decades demonstrates that for a number of long-lived radionuclides, soil-to-plant transfer factors show variations which may exceed three orders of magnitude (Coughtrey and Thorne 1982; Frissel 1992). For radiocesium uptake from agricultural soils, transfer factors show ranges of up to three orders of magnitude even for individual soil–crop combinations (Nisbet and Woodman 2000).

The reason for the high variability of soil-to-plant transfer factors is obvious. This macroscopic parameter integrates a number of soil's chemical, biological, hydrological, and physical processes and plant's physiological processes, each of which shows its own variability and in addition may be influenced by external factors such as climate and human agricultural practices. Evaluation of the influence of these processes has been attempted by statistical inference from soil-to-plant transfer factor databases (Van Bergeijk et al. 1992; Sheppard and Evenden 1997; Nisbet and Woodman 2000) but with moderate success.

3.1 Soils

Many types of soil exist (UNFAO 1998) because of the wide range of biological, geological, and climatological conditions. Major classes in which soils are grouped on the basis of texture are gravel, sand, silt, and clay. In addition, the term loam is widely used for certain combinations of sand, silt, and clay. In soil classification for agricultural purposes, loam indicates a certain distribution of particle sizes. Soils of dry regions normally have pH values of about 7, and the usual order of abundance of exchangeable cations in the soil is Ca > Mg > I > Na. Soils of humid regions usually have pH values below 7, and under conditions of extreme leaching, hydrogen may represent 90 % or more of the total exchangeable cations. The usual order of abundance of exchangeable cations in humid regions is H = Ca > Mg > K > Na.

Table 2 summarizes the effects of key soil parameters on the mobility of some elements with important radionuclides, and the specific behavior of these elements is described below.

3.2 Radionuclide Dependence

Table 3 shows the TF AM and GM values for the principal radionuclides without differentiating between plant and soil types. The TF values show a very wide variability. Differences in the order of a factor of 2 were found for Co and Zn, but as high as a factor of 5 for Cs and Ra. For GM values, the following sequence was found: TFZn > TFSr > TFCs ≅ TFCo > TFRa ≅ TFU > TFPb ≅ TFI.

3.3 Influence of Plant Group

The distribution of TF for some plant groups was reviewed (IAEA 2010). In Fig. 4, the values of TF obtained for three plant/plant part groups are shown, distinguishing the data obtained for different soil types. For rice, in spite of the TF GM being lower in clay soil, no significant differences in TF distribution were observed for the different soil types. Leafy vegetable TF values from clay soil

Table 2 Influence of soil characteristics on the behavior of different radionuclides in soils (compiled from Bunzl 1987; Coughtrey et al. 1983; IAEA 1994; Mortvedt 1994)

	Cs	Sr, Ra	I	U, Pu	Ru
Similar ions	K, Rb, NH^4	Ca, Ba		Np	Tc, Mo, Nb, Zr, Y, Co, Fe, Mn, Cr
Chemical form in soil	Cs^+	Sr^{2+}	I_2, CH_3I, I^-, IO_3^-	PuO_2^{2+}, $Pu(NO_3)^{3+}$	$RuNO^{3+}$, Ru^{3+}, RuO_4^-
	Changes in RN mobility and plant availability if…				
pH value decreases	↑	↑		↑	↑
Clay content decreases	↑	↑		↑	↑
Sand content decreases	↓	↓		↓	↓
Humus content lowers	⇔	↓	↑	↓	⇔
CEC decreases	↑	↑			↑
K_d value (1 kg^{-1})	10^2–10^3	10^1–10^2	10^{-1}–10^2	10^2–10^3	10^1–10^3

Key ↑ increased mobility; ↓ decreased mobility; ⇔ no clear effect

Table 3 Principal radionuclides in tropical and subtropical database (IAEA 1994)

Rad.	Tropical			Subtropical		
	N	AM	GM	N	AM	GM
Cs	299	1.52E+00	1.97E−01	495	3.29E+01	5.28E−02
Sr	149	3.17E+00	8.43E−01	299	5.48E−01	1.80E−01
Co	104	3.34E−01	1.78E−01	83	2.36E+01	4.33E−02
Zn	133	2.22E+00	1.21E+02	64	1.14E+00	4.70E−01
Ra	282	2.46E+00	5.96E−02	–	–	–
U	148	2.28E−01	5.70E−02	–	–	–
Pb	70	1.37E−01	1.26E−02	–	–	–
I	–	–	–	63	3.62E−01	1.20E−02

demonstrate a larger transfer factor than loam and sand soils. The main conclusions obtained are as follows:

- A wide TF value variability was found for all radionuclides when plant and soil groups were not distinguished. The difference in the order of magnitude of TF value ranged from 2 (Co and Zn) to 5 (Cs and Ra).
- When different plant group/plant part combinations are considered, TF value variability is markedly lower.

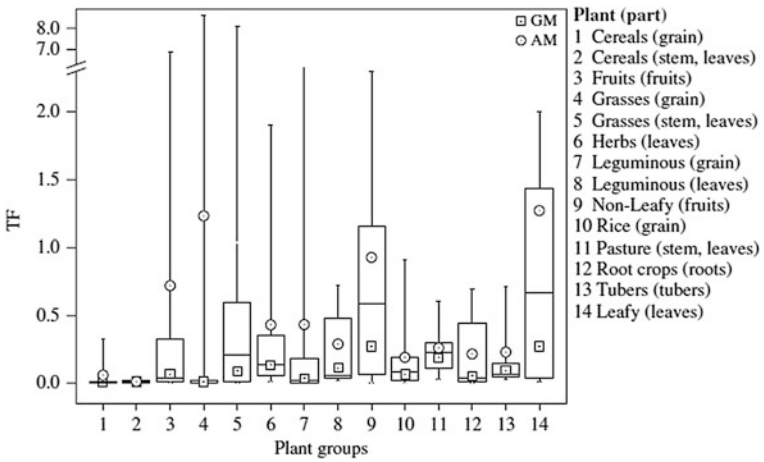


Fig. 4 Box chart representation of TF for Cs for different plant groups. GM and AM indicate geometric and arithmetic mean values, respectively

- It was found that for many combinations, TF values are reasonably fitted by a lognormal probability distribution.
- In most plant groups, Zn and Sr have the highest TF values. Ra and U have low TF values, and the TF is lowest for Th. A relatively high TF was found for Ra in grasses. TFs for Cs have intermediate values.
- Leguminous and leafy vegetables have the highest TF values, while for grains, particularly rice, transfer factors are lower.
- Soil type seems not to have a decisive influence on TF values. Only the Cs TF value in tubers grown in sand soil has a noticeably higher value than TF values obtained from clay and loam.

3.4 Comparison of TF Values Derived from Pot, Lysimeter, and Field Experiments

In some evaluations of soil–plant transfer data for agricultural crops, pot experiments turned out to yield different average values when compared with data observed under field conditions. According to Frissel et al. (1990), the reasons for this observation are as follows.

- A more intensive exploration of the contaminated substrate by plant roots due to the limited space available in plant pots.
- In pot experiments, soils are mostly contaminated artificially using radionuclides in easily soluble form (dissolved in aqueous solutions). Binding to the soil substrate can increase with time (aging effects), until equilibrium conditions are reached.

- To avoid plant drought stress, plant pots have to be irrigated regularly as the limited soil volume and high root density result in rapid water loss by evapotranspiration.

These differences can be reduced to a minimum by choosing an experimental design which allows enough space per plant for the root system and some equilibration time after artificial contamination. The differences between the data are within the normal range of variability, and a systematic bias to higher TF values for pot experiments was not observed.

The IAEA, together with the United Nations Food and Agriculture Organization (UNFAO 1998) and the International Union of Radiologists (IUR), conducted a Coordinated Research Project (CRP) on Transfer of Radionuclides from Air, Soil and Freshwater to the Food chain of Man in Tropical and Subtropical Environments. This produced a set of values for key transfer parameters of radionuclides between the various components of tropical and subtropical ecosystems that can be used in dose assessment models. It concentrated on what are considered as the key parameters in assessment models—radionuclide transfer from soil to plant and from freshwater to fish. A data bank was developed from transfer factors for radionuclides, principally ^{137}Cs and ^{90}Sr, from soil to cereals, fodder crops including grass, legumes, root crops, green vegetables, and plantation crops. Account was taken of soil properties, nature of the contamination (artificial, weapons testing fallout, Chernobyl fallout, and so on), and the type of experiment (field, pot, or lysimeter) that generated the values. For soil-to-plant transfer, the following conclusions were drawn:

- there are no systematic differences between soil-to-plant transfer factors in temperate, subtropical, and tropical environments;
- the effect on transfer of (a) soil pH, (b) nutrient status of the soil, and (c) time elapsed since the soil was contaminated with radionuclides is generally independent of the climatic zone;
- there exist, however, ecosystems with a relatively high or low uptake (by a factor of 10 or even 100 higher or lower than average values);
- a higher or lower uptake condition is nuclide specific; an ecosystem may show a relatively high or low uptake for a particular radionuclide and not at all for other radionuclides;
- a higher or lower uptake condition is *not* crop specific. If an ecosystem shows a relatively high or low uptake for one crop, all crops show this behavior qualitatively.

The earlier CRP Transfer of Radionuclides from Air, Soil and Freshwater to the food chain of Man in Tropical and Subtropical Environments concluded that the generic values as published in the IUR/IAEA Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments (IAEA 1994) may be used as a first approximation in assessment studies, but that site-specific deviations of a factor of 10 or more must be expected. For more precise assessment studies, an investigation to identify the conditions causing local deviations is necessary.

The investigators reported almost 3,000 TF values, mostly for radioisotopes of Cs and Sr but also of Mn, Zn, Po, Pb, Th, U, and K, obtained in some 25 soil lower-level units from 16 different soil groups using 25 crops. Geometrical means were used because data in the literature consistently show lognormal distributions. It is stressed that the mean values consider all observations even in cases where it might seem advisable to reject certain observations. This appendix also contains data for other nuclides and includes information about soil properties and crops. The data sheets from which they were calculated are available at ftp://iaea.org/dist/rifa-trc/Crete/RCM/Frissel/raw-data/.

Greenhouse experiments were conducted to investigate the dependence of ^{54}Mn, ^{60}Co, ^{85}Sr, and ^{137}Cs transfer from sandy soil to soybean plants on the growth stage when a radioactive deposition occurs. A solution containing ^{54}Mn, ^{60}Co, ^{85}Sr, and ^{137}Cs was applied onto the soil surfaces in the lysimeters at six different times—2 days before sowing and 13, 40, 61, 82, and 96 days after sowing. Soil-to-plant transfer was quantified with a transfer factor ($m^2\ kg^{-1}$ dry) specified for the deposition time. The transfer factor values of ^{54}Mn, ^{60}Co, ^{85}Sr, and ^{137}Cs for the seeds were in the range of 1.5×10^{-3}–1.0×10^{-2}, 4.7×10^{-4}–3.2×10^{-3}, 5.7×10^{-4}–1.0×10^{-2}, and 3.0×10^{-5}–2.7×10^{-4}, respectively, for different deposition times. The corresponding values for the leaves were 6.4×10^{-3}–3.2×10^{-2}, 4.3×10^{-4}–2.0×10^{-3}, 5.1×10^{-3}–5.3×10^{-2}, and 9.2×10^{-5}–1.9×10^{-4}, respectively. The values for the seeds were on the whole highest following the middle growth stage deposition. After the presowing deposition, the transfer factor values of ^{54}Mn, ^{60}Co, and ^{137}Cs for the seeds decreased annually, so those in the fourth year were 53, 75, and 34 % of those in the first year, respectively. The present results may be useful for predicting the radionuclide concentrations in soybean plants due to their root uptake following an acute soil deposition during the vegetation period and for validating a relevant model.

4 Classification of Soils Based on TFs

4.1 Soil Classification

Soil classification involves a range of criteria, but pedological considerations dominate. It assesses the essential properties of the soil itself including the processes of formation, distribution, mineralogical composition, the organic matter content, and the texture. There are 30 soil groups:

Acrisols; Albeluvisols; Alisols; Andosols; Anthrosols; Arenosols; Calcisols; Cambisols; Chernozems; Cryosols; Durisols; Ferralsols; Fluvisols; Gleysols; Gypsisols; Histosols; Kastanozems; Leptosols; Lixisols; Luvisols; Nitisols; Phaeozems; Planosols; Plinthisols; Podzols; Regosols; Solanchaks; Solonetz; Umbrisols; and Vertisols. They are further subdivided into 121 lower-level units, several of which may occur in the same soil group so that 509 group/unit combinations are listed in (UNFAO 1998). It is at the unit level that criteria include some of agricultural significances such eutric (fertile defined as >50 % base saturation), dystric (unfertile, <50 % base saturation), and calcaric (calcareous). However, soils influenced by human activity may be placed in the Anthrosol group. Given the secondary level of significance allocated to agricultural properties, it cannot be assumed that this classification will be the most appropriate for the prediction of TFs, but clearly, it must be taken into consideration.

4.2 Weather

Weather data were not systematically collected although most investigators record some details in their reports. There is no obvious procedure with which to assess the effect of weather on the TFs measured in such a relatively small data set. Djingova et al. (2005) found that TFs to winter cabbage were higher than those to summer cabbage, presumably because it takes longer for the winter crop to reach maturity, an indirect effect of weather. Schuller et al. (2002) noted that TFs to chard, which is cut several times per season, declined through the year although it is not clear whether or not this should be interpreted as a weather effect.

4.3 Crop Variety

Skarlou et al. (2003) found that TFs to cabbage variety Brunswick from soils were 2.5, 1.3, 1.3, and 2.2 times those to variety Kozanko, and corresponding figures for sweet corn cultivars Vilmorin and Elite were 1.3, 0.5, 2.8, and 2.2, so in these cases, the effect was relatively small.

4.4 The Influence of Soil Properties on Cs Reference Transfer Factors

Table 4 shows reference TFs derived from the IUR database and values obtained in the earlier CRP (Frissel et al. 2002). This combined data set is larger than that obtained in new CRP, so any classification developed here should therefore not conflict with this table. Unfortunately, with a few exceptions, soil groups as defined by the FAO classification are not listed in the IUR database and most investigators are no longer available. With the earlier CRP, the situation is better, but not optimal. Also, in most cases, the IUR database does not include exchangeable K. Only, the soil texture is almost always reported, as is the notation, P, for peat soils, i.e., histosols in the FAO classification. Further, it would be desirable to estimate the influence on TF of different conditions such as the time

Table 4 Reference transfer factors of Cs for cereals under equilibrium conditions (Bq kg^{-1} dry crop)/(Bq kg^{-1} soil in the upper 20 cm of soil)

	Nutrient status of soil	Soil texture	Reference expected value	TFs of Cs range
Soil group 1	High $pH > 4.8$	All soils	0.006	0.002–0.01
Soil group 2	Medium $pH > 4.8$	Clay and loam soils	0.03	0.01–0.1
		Sand, peat, and other soils	0.05	0.02–0.1
Soil group 3		Clay soils	0.2	0.1–0.5
		Sand and other soils	0.3	0.1–1
	Very low or $pH < 4.8$	$pH > 4.8$	0.3	0.1–1
		Peat soils $pH > 4.8$ Normal moisture	0.6	0.2–2
		Wet, gleyic	3	1–10
Soil group 4	Soils with exchangeable $K < 0.05$ cmol(+)/kg		20	10–50

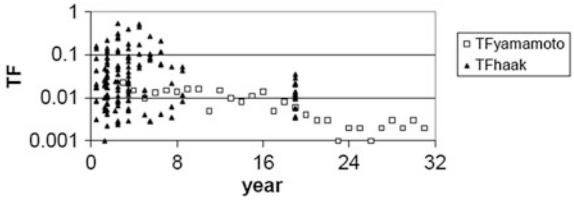


Fig. 5 Influence of the time elapsed since the Cs contamination of soil on the TF for cereals. *Legend* TFyamamoto = FAO/IAEA/IUR Workgroup collected data by Yamasaki, TFhaak = IUR data bank (available at ftp://iaea.org/dist/rifa/Crete/RCM/Frissel). TF in (Bq kg^{-1} crop)/(B kg^{-1} soil)

that radionuclide was in contact with the soil, fertilization, irrigation, soil management, and the weather, but these factors were not systematically recorded.

4.5 Contact Time and Fixation

Fixation of Cs is a serious problem. Fixation is the partly irreversible, slow adsorption of Cs, especially to clay minerals. Usually, fixation is most important in the first few years after contamination of the soil, but the amount that will be fixed differs from soil to soil. The process may continue for a long time, but the kinetics of the process have not been characterized numerically. One would hardly expect to see fixation effects on soils contaminated after the Chernobyl accident which occurred 13–15 years before the measurements were taken, and the results of Sanzharova and Prister are broadly consistent with this view. Similar changes occur in other data sets (Fig. 5).

4.6 Time Trends

Radionuclides can be released and deposited onto soils at any time of the year. The physiological activities of plants, the developmental stages of their organs, and the availability of radionuclides for root uptake change with time (Choi et al. 2005, 2009). In the case of an acute release during the vegetation period, therefore, soil-to-plant transfer of radionuclides may greatly depend on the time of their deposition. Accordingly, time-dependent deposition values of a soil-to-plant transfer factor would be useful for estimating the root uptake from an acute vegetation–period deposition (Choi et al. 1998, 2009).

Transfer factors of radiocesium and radiostrontium in lysimeter and field experiments were frequently observed to decrease slowly with time for some years after contamination of the soils (Squire and Middleton 1966; Noordijk et al. 1992; Nisbet and Shaw 1994). Commonly, this time dependency is attributed to a slow irreversible fixation of the radionuclides to the soil matrix (IAEA 1994). Following the work of Cremers and coworkers (Cremers et al. 1988), a long-term decrease in radiocesium uptake by plants most often is attributed to its sorption and fixation to clay minerals (Shand et al. 1994; Hird et al. 1996). From the long-lived radionuclides, cesium (^{134}Cs and ^{137}Cs) and strontium (^{89}Sr and ^{90}Sr) isotopes burden the environment for greater time period.

Soil-to-plant transfer of various radionuclides is known to be affected by soil properties, plant species and variety, climatic condition, and cultural practices (Papanikolaou 1972). Variation of the concentration of radionuclides on the soil surface depends mainly on its mineralogical composition, its chemical and physical properties, meteorological conditions, and the possible transfer of material to deeper soil layers (Missaelidis et al. 1987; Vosniakos et al. 1998). The possibility of fixation of Cs isotopes by geological material and soil has been the subject of previous studies (Sikalidis et al. 1988). The mechanism of fixation depends strongly on the mineral composition of the soil. The existence of ^{137}Cs in the soil is important because of its possible transfer to the cultivated plants and eventually to animals and humans. It also increases the direct-exposure doses received by humans from terrestrial natural radioisotopes by 10 % (Kritidis and Kollas 1992). The transfer of Cs is also increased with increasing organic matter content.

4.7 Classification by Cs TFs

As stated earlier, any new classification should not conflict with Table 4. They include all Cs TF values for soil units of the CRP which correspond with groups 1 and 2 of Table 5. Maximum and minimum values for expected TF values were fitted by eye. They form the core of this classification. For soils in group 1, TF seems not to be related on texture, but in group 2, TFs, which are considerably

Table 5 Classification of soils by Cs TFs

Soil group	Expected transfer factors for Cs (Bq kg^{-1} dry crop)/(Bq kg^{-1} dry soil upper 20 cm)	
1 Cambisol, Chernozem, Ferralsol Fluvisol	Lower limit	0.001
Gleysol, Kastanozem, Leptosol, Phaeozem, Vertisol	Upper limit	0.015
2 Podzol, Luvisol, Andosol, Acrisol, Nitisol	Lower limit	0.005
	Upper limit clay	0.1
	Upper limit sand	0.2
3 Histosol	Lower limit	0.005
Humic soils, Histic soils	Upper limit	0.5
4 Albic, Arenosol	Upper limit	5
5 Less suitable soils	Upper limit	High

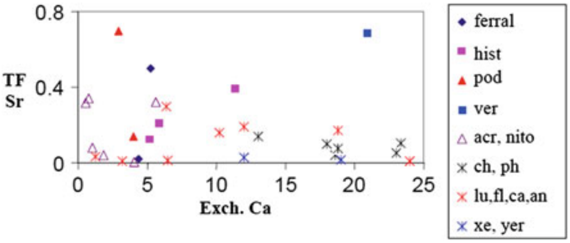


Fig. 6 TFs as a function of the exchangeable Ca

higher, seem to be related to the texture. This is in agreement with the groupings in Table 5, but their nutrient status was a leading criterion, whereas here soil units are used. These considerations lead to the following classification of soils for the uptake of Cs by cereals (Table 5).

As discussed earlier, this classification is imprecise because many of the TF measurements included values obtained before complete equilibrium of Cs distribution in the soil had been reached and only limited data are available for many soil groups. Consequently, the lower limits of expected TFs for groups 2 and 3 are the same and overlap the range of group 1. However, for planning purposes, it would be prudent to use the upper limits in which case there are reasonably clear distinctions. Therefore, these results give promise that soils could be classified in this way, but very many additional data are required for confirmation.

4.8 The Reference TF for Strontium

In addition to pedological considerations, properties such as organic matter, soil acidity, calcium carbonate content, and texture are used to define many soil groups and lower-level units. All these properties influence the uptake of Sr, so it should be possible to group soil units on the basis of reference Sr TF values. Figure 6 shows the TFs as a function of the exchangeable Ca.

Fig. 7 Relation between soil texture and Sr TF

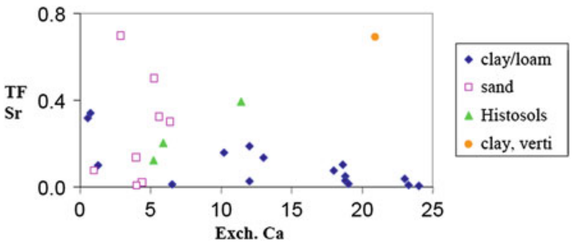


Table 6 Classification of soils based on Sr TF

Group 1		Expected transfer factors for Sr (Bq kg^{-1} dry crop)/(Bq kg^{-1} dry soil upper 20 cm)		
Acrisol	Andosol	Texture	Exch. Ca	Range TF
Cambisol	Chernozem	Clay and loam	0–2	0.01–0.4
Luvisol	Nitisol		20–20	0.01–0.2
Fluvisol	Phaeozem		>20	0.01–0.1
Gleysol	Ferralsol	Sandy soil	0–10	0.01–0.8
Podzol			>10	0.01–0.3
Group 2				0.01–0.4
Histosol				
Group 3		???		0.01–0.8
Vertisol				

The scheme in Table 5 uses clay, sand, and peat contents as the main criteria. Therefore, Fig. 7 distinguishes TF values on this basis. For clay/loam and sand histosols, it gives a reasonable fit. The vertisol does not follow the general trend, but it concerns one only. Fig. 7 is not very conclusive because it does not contain enough observations. IUR data do not include exchangeable Ca; therefore, only the mean value of the TFs for each soil texture is given. The agreement for clay/loam and sand soils is good, but it is poor for peat soils (not shown).

4.9 Classification by Sr TFs

The foregoing considerations lead to the following classification of soil for the uptake of Sr (Table 6).

There were enough data sets to give a fair insight into the behavior of Cs for some soil units (fluvisols, luvisols, chernozems, and podzols), but others were only represented by one set of data. It is possible that one set of data is not representative. It was assumed that all lower-level units belong to the same soil group, but there is no proof. From some units, there was no representative at all. With soil group 1 (Cs classification), the majority of data refer to old contaminations, while for soil group 2, the data refer to recent contaminations; this could have unbalanced the choices made. The Sr classification is based on very limited data, and in addition, the measurement of Sr in some cases contained a large degree of uncertainty. The range of TFs is rather wide; the higher the values occurring with the most acid and dystric classes, the lower the values occurring with the calcaric and eutric classes. At the moment, there is not sufficient information to go into more detail. Within soil group 2 (Cs classification), there are two eutric and one dystric units listed. The TF of the latter unit is lower than that of the former two, but one cannot derive a rule from three sets of observations. One might think of a statistical analysis within a soil group, but lack of quantitative data on the individual factors affecting TF values precludes this. Despite this, the CRP made a successful beginning with the classification, and it is worthwhile to consider possible applications.

A classification of soil ecosystems might be a way to reduce uncertainties due to the enormous range of uptake parameters. Our contribution is to produce data on transfer factors of ^{134}Cs from soil to reference plants in a range of Bangladeshi soil systems to characterize systems in which TFs might differ substantially from what would be regarded as normal. The comparison between the results is obtained for TF of ^{137}Cs for wheat (grain and straw) during the 4 years of the experiment. The results can be summarized as follows:

- The TF observed for wheat (grain and straw) grown in soil type 1 was higher than for soil type 2.
- The TF for straw is higher than for grain as expected (e.g., Nisbet and Show 1994). The trends in the TF change with the time after contaminations are the same.
- The TF decreases with the time as expected for plants grown on soil type 1. Obviously, fixation of radiocesium takes place during the first year. According to the data obtained by this study, the TF values remain practically constant for the next 2 years within the biological variations. This coincides with the opinion of Frissel et al. (2002) that 1 year might be generally enough time for ^{137}Cs soil fixation, although for "safety" reasons, 4 years are to be considered.
- TF for plants on soil type 2, however, increases after the first year to return to the first-year results after the second year and the third year. Similar effects were established in Massas et al. (2002) for other crops. Obviously, for this type of soil, equilibrium for Cs is reached after a longer period, although the higher elite content suggests quicker fixation.
- Although the general expectation is that TF values follow lognormal distribution (e.g., Sheppard and Evenden 1990), the investigation of the skewness (a), defined as $a = \sqrt{2}(\ln E - \ln M)$ (M median, E average), proved that the distribution of the TF in the present study tends to be normal (the value of a is <0.3).
- The present TF value for soil type 1 is very near to the reference TF values, published by IAEA (1994), Frissel et al. (2002). For soil type 2, however, the

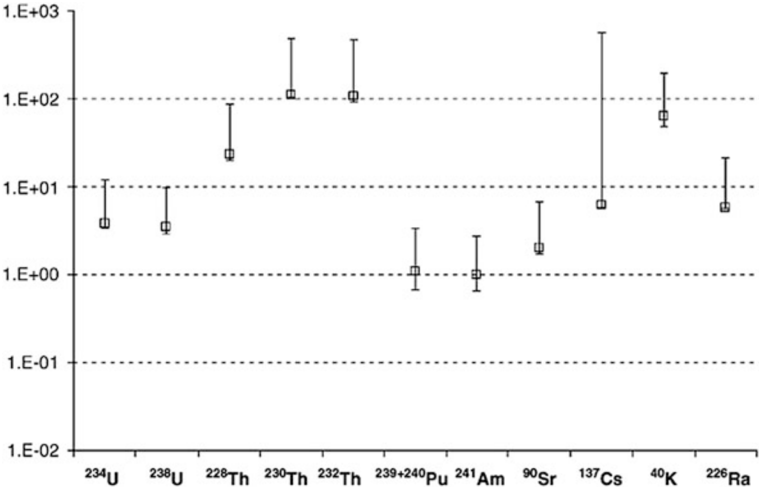


Fig. 8 Median and range of available transfer factors (TF) for artificial and natural radionuclides for several species of mushroom (Baeza et al. 2004)

TF is within the IAEA interval and just below the lower limit of the range of Frissel et al. (2002). It is quite obvious that further refinement of the soil classification should be done using soil types and parameters because according to the preliminary classification in Frissel et al. (2002), both the investigated soils fall within the same group on the basis of nutrient status. Evidence in this direction is the variation of the TF values (more than 10-fold) in both IAEA (1994), Frissel et al. (2002).

- The TFs of potassium calculated for both the investigated soils show practically identical values, which obviously is due to the nutrient function of this element, and therefore, its uptake by the plant is not seriously influenced by the soil properties.

The transfer of radionuclides (^{137}Cs, ^{40}K, ^{226}Ra, ^{90}Sr, $^{239+240}$Pu, and ^{241}Am) had also been analyzed in previous work (Baeza et al. 2005, 2006). Compared to the uranium and thorium TF values, those of ^{137}Cs were generally higher, those of ^{40}K, ^{226}Ra, and ^{90}Sr were similar or a little higher, and those of $^{239+240}$Pu and ^{241}Am were similar (Fig. 8).

Given the medians and ranges of the available transfer for mushrooms, the efficiencies of the radionuclide transfers were ranked as follows:

$$
\begin{aligned}
&{}^{228,230,232}\mathrm{Th} \approx {}^{40}\mathrm{K} \geq {}^{137}\mathrm{Cs} \geq {}^{234,238}\mathrm{U} \\
&\approx {}^{226}\mathrm{Ra} \geq {}^{90}\mathrm{Sr} \geq {}^{239+240}\mathrm{Pu} \approx {}^{241}\mathrm{Am}.
\end{aligned}
$$

The migration and distribution of radiocesium in the soil profile varies depending on soil properties such as soil texture, organic matter content and pH and on climatic conditions, land use, and management practices. Important factors affecting the transfer of radiocesium to crops/plants are the distribution of the root system in the soil profile as well as the soil pH and nutrient status (IAEA 2010).

Both soil and plant samples of nine different plant species grown in soils from southeastern China contaminated with uranium mine tailings were analyzed (Chen et al. 2005) for the plant uptake and translocation of ^{238}U, ^{226}Ra, and ^{232}Th. Substantial differences were observed in the soil–plant transfer factor (TF) among these radionuclides and plant species. Lupine (*Lupinus albus*) exhibited the highest uptake of ^{238}U (TF value of 3.7×10^{-2}), while Chinese mustard (*Brassica chinensis*) had the least (0.5×10^{-2}). However, in the case of ^{226}Ra and ^{232}Th, the highest TFs were observed for white clover (*Trifolium pratense*) (3.4×10^{-2}) and ryegrass (*Lolium perenne*) (2.1×10^{-3}), respectively. In general, the TFs across all plant species for the three radionuclides were in the following order: $^{238}\text{U} \sim {}^{226}\text{Ra} > {}^{232}\text{Th}$.

5 Conclusions

Chemical properties, especially similarities with nutrient elements, determine the extent to which anthropogenic radionuclides will become involved in terrestrial nutrient cycling. Long-lived radioisotopes of cesium and strontium have received the greatest attention due to their similarity with K and Ca and hence bioavailability and their level of global deposition. Due to the focus of most studies on the human food chain, the best understood processes are those important for the soil-to-plant and plant-to-animal transfer. Due to the inherent complexity and spatial variability of the soil-plant system, the uptake of radionuclides in vegetation from soil is difficult to quantify. The transfer factor (TF) is a useful parameter, which is usually used for evaluating the impact of releases of radionuclides into the environment. The TF depends on the vegetation type, soil properties, and the type of radionuclides. The factors that determine the variation of radionuclide activity with depth in soil profile are rainfall intensity, pH, organic matter content, soil moisture content, soil texture, soil structure, infiltration rate, sorption characteristics of the particular radionuclide, land use, and management practices. Generally, the soil-to-plant transfer of radionuclides depends on soil type, pH, solid/liquid distribution coefficient, exchangeable K^+, and organic matter contents. Absalom et al. (1999, 2001) presented a model that predicts the soil-to-plant TF of radionuclides (clay content, organic carbon content, exchangeable potassium, and pH). The Absalom model has been tested in Europe with successful prediction of the fate of Chernobyl and weapons fallout of ^{137}Cs. However, testing and validation of this model for the tropical food chains in many countries in South Asia is very limited. As countries in the South Asian region like Bangladesh is expanding applications of nuclear technology, a comparable model is required to predict the impact of deposited radionuclides based on the regional parameters derived for wet–dry tropical environments. In order to apply the Absalom model and/or to modify the model, regional databases for model validation need to be developed for the tropical environments. There are two promising alternative approaches to classifying soils with regard to radionuclide behavior. One uses correlation and factor analysis to identify the most important soil properties controlling TFs which can then be used predictively. The other is a semiempirical procedure based on the assumption that ion exchange capacity, pH, and organic matter content control ion availability in the soil.

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Contributions to the State of the Art in Radionuclides–Plants Interaction Field

Manuela Murariu, Gabi Drochioiu, Alexandru Cecal and Karin Popa

Abstract Phytoremediation is an option considered in the radioactive pollution of soils and waters as an easy, environmental-friendly, and energetically inexpensive method in order to clean radioactive-contaminated fields or surface waters. A short review of radionuclides uptake at laboratory scale, greenhouse, and in-field is presented, and our results are highlighted. In a model study, wheat germination is presented here as a cleaning method at laboratory scale and a number of toxicological and biochemical aspects are further discussed. The effect of several natural and synthetic radioprotective agents is also presented.

Keywords Biochemistry · Phytoremediation · Radioactivity · Radioprotective agents · Toxicology · *Triticum aestivum* L.

Contents

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1 Introduction

Ionizing radiation may provoke mutations in plants, which leads to common, low-specific physiological and biochemical changes in plant organisms; the most common from them could be inhibition of root growth, changes in enzyme activity, membrane damages, etc. (Polischuk et al. 2005). Generally, the deposition of the anthropogenic radionuclides from air to landscape originates from the nuclear weapon tests or nuclear facilities such as nuclear reactors (Alexakhin 1993; Kobashi 2009). For instance, the deposition of ^{137}Cs fallout on the surface of the earth had a peak in the first half of the 1960s (nuclear tests explosions) and then has been decreased, except for the temporary increases due to the Chernobyl and Fukushima accidents (Igarashi et al. 2003; Steinhauser et al. 2014).

Most of the literature data on the radioactive remediation of the environment is focused on the microbes—radionuclides interaction (see, e.g., Cecal et al. 1997; Liu et al. 2010). Biomass has a remarkable capability for adsorbing radioactive ions and heavy metals, because its content of electron-donating functional groups or ligands such as like carboxyl, hydroxyl, amide, or phosphoryl groups (De Philippis et al. 2011). The biosorption of UO_2^{2+} ions on some green algae (Cecal et al. 2012a, b) or yeasts (Popa et al. 2003; Tykva et al. 2009) has also been investigated.

Experiments on the removal and recovery of U(VI) from aqueous solution by tea waste have been conducted as well, and the adsorbent was characterized by scanning electron microscope and energy dispersive spectrometer before and after the adsorption treatment (Ding et al. 2012). Certain plants were found to display a high affinity toward the radioactive cations and consequently have been selected for treatment of contaminated water (Dushenkov et al. 1997).

In the case of dispersed radioactive contaminations, IAEA proposed three solutions, as a function of a number of factors influencing the technology selection (e.g., sources, effectiveness, cost, occupational safety and health, socioeconomic consideration): non-intervention, containment, and removal (IAEA Technical Report Series No. 424 (2004), 442 (2006)). In the first scenario, phytoextraction/ phytoremediation is one of the most effective mechanisms. Thus, long-lived radionuclides can be effectively removed from the soil only by harvesting of vegetation (Gouthu et al. 1997).

Currently, there is only limited information on the long-term environmental impact of the Fukushima Dai-ichi nuclear accident (Hirose 2012). The recent radioactive leak from the Fukushima Dai-ichi NPP into the sea reminded the public and authorities that radioactive contamination of the seawater with medium-lived ^{137}Cs and ^{90}Sr is still a special and actual concern. The impacts of radionuclides from this accident on the ocean have been investigated by Buesseler et al. (2011). The authors studied the radioactive isotopes of iodine and cesium in ocean water and found a minimal impact on marine biota or humans due to direct exposure in surrounding ocean waters, although the level of some radionuclides was significantly elevated.

Since large amounts of radionuclides were released from the Fukushima Daiichi nuclear accident, soil radiocesium contamination of rice fields in Aga and Minamiuonuma, Niigata, 130 and 200 km away from the power plant, respectively, has been investigated (Harada and Nonaka 2012). The higher concentrations were found in the upper soil layers, suggesting that spring tillage, and flooding performed before rice transplantation do not disperse radio cesium. Besides, radioactivity levels in rice fields may also be elevated by an influx of additional radionuclides, probably in irrigation water.

Radionuclide remediation through plant is a continuous developing field. In metal ions accumulation studies with plants, it is generally accepted that the uptake have two steps (Cho et al. 1994): the first one is a rapid binding to negatively charged groups on the cell surface and a passive transport of metal ions through the cell wall during a short time, while second step involves penetration through the cell membrane and the bioaccumulation of the metal ions onto the protoplasts (Cecal et al. 2001). In the first step, part of the ions are attached to the membrane by chemical processes but other part is presented in the surface film adhering to the cell membrane and in the cellular free space (Wolterbeek et al. 2000).

Under such circumstances, this work highlights our previous contributions on the uptake of radionuclides in laboratory, greenhouse, or in-field conditions, as well as on the newly proposed wheat germination experiment used to assess the toxicological, biological, and biochemical mechanisms that make phytoremediation work. Besides, the effect of radioactive ions on the plant physiology, as well as their accumulation in different parts of plant organisms is highlighted.

2 Contributions to the Field

Our group devoted an important amount of time to the study of the radionuclides uptake from wastewaters or contaminated soils at laboratory scale and in-field during the past 15 years. Thus, accumulation of naturally occurring radioisotopes as well as relevant radioisotopes of anthropological origin by plants was studied in specific systems. Moreover, different radioactive tracers were used in order to conclude on biochemical mechanisms involved in heavy metals uptake by plants.

In a seminal paper, the accumulation kinetics of $^{60}Co^{2+}$ and UO_2^{2+} from simulated wastewaters on *Pistia strationes*, *Riccia fluitans*, and *Lemna minor* (duckweed) were studied (Cecal et al. 1999). Later on, the topic was extended to the $^{204}Tl^{+}$ uptake by *L. minor* (Cecal and Popa 2001). The distribution of radioactive ions $^{137}Cs^{+}$, $^{60}Co^{2+}$, and $^{51}Cr^{3+}$ in various cell components extracted from the above-mentioned hydrophilic plants is presented in Cecal et al. (2002a). The results show an intense activity of the polysaccharide and lipoid fractions in bioaccumulation process.

The living *L. minor* vascular plant and two different sorbents obtained by chemical treatment of this plant were tested in order to study the removal process of $^{60}Co^{2+}$, $^{65}Zn^{2+}$, and $^{55+59}Fe^{3+}$ from low radioactive wastewaters (Popa et al. 2006). The most effective sorbent was the protonated biomass, indicating the decisive contribution of the complexation process in the assembly of the uptake mechanisms. The uptake performance of the biosorbent obtained from the *L. minor* was increased with about 20 % by treatment with nitric acid. In respect with the metabolically active mechanism, it was noticed the slow desorption of $^{65}Zn^{2+}$ and the continuously increase of $^{55+59}Fe^{3+}$ uptake degree. The Na_2CO_3 generated in situ in systems participates to a double exchange reaction with the metallic cations during the uptake. $^{60}Co^{2+}$, $^{65}Zn^{2+}$, and $^{55+59}Fe^{3+}$ radiocations prefer to coordinate N-donor ligands at the expense O-donors ones. A parallel study deals with a laboratory experiment on the bioleaching of a poor uranium ore by *L. minor* and *R. fluitans* under various operating conditions (Cecal et al. 2002b). It was found that the bioleaching has its origin in the "in situ" oxidizing role of the atomic or molecular oxygen resulting from the photosynthesis process on the species of uranium in intermediate oxidizing states, according to the chemical reaction:

$$UO_2 + O + 2H^+ = UO_2^{2+} + H_2O \tag{1}$$

The uranyl (dioxouranium) ion amount accumulated in the plants is negligible as compared to the dissolved one, owing the ionic competition between uranyl and the biocations presents into the system. The X-ray diffraction patterns prove that the U(IV) presented in pyrochlore mineral are completely oxidized to U(VI), while U(IV) from thucholite is only partially oxidized, in the presence of the considered plants.

Uptake, biotransformation, and elimination of ^{99}Tc in duckweed are reported by Hattnik et al. (2003). Mkandawire and Dudel studied the uranium (Mkandawire and Dudel 2002) and arsenic (Mkandawire and Dudel 2005) accumulation by *Lemna gibba* L. under natural conditions (tailing waters of abandoned uranium mining sites in Saxony, Germany). Thus, due to the wide range of applications in the field and to the cumulative favorable factors, duckweed bioassay is currently considered as one of the most standardized bioassays for assessing the impact of contaminants in aquatic environments (Mkandawire and Dudel 2007; Mkandawire et al. 2014).

It was also proved that *Azolla caroliniana* Willd. water fern can potentially and efficiently remove the man-made, medium-lived radioisotopes $^{137}Cs^{+}$ and $^{60}Co^{2+}$ efficiently from dilute wastewaters through bioaccumulation and/or absorption on the acid-treated form of the biomass obtained from the above-mentioned fern (Popa et al. 2004). Under the selected working conditions, the equilibrium was attained after about 2 h contact time and the maximum values of the distribution coefficients were 1,900 for $^{60}Co^{2+}$ and 99,900 for $^{137}Cs^{+}$, respectively (total uptake); these values were obtained using the protonated biomass. The capacity of radioactive ions accumulation was affected by the presence of radioactive competitive cations. Both chemical toxicity and radiotoxicity of some radioisotopes like gamma-emitting cesium and cobalt on the wheat germination have been investigated (Popa et al. 2008b).

A two-year field survey of ^{226}Ra translocation from soil to selected spontaneous plants (*Mentha piperita*, *Urtica dioica*, *Fragaria vesca*, *Tussilago farfara*, *Dryopteris filix-mas*, *Cirsium arvense*) growing in the Crucea (Romania) uranium mining area was conducted by Popa et al. (2008a). The ^{226}Ra translocation from soil was affected by analyzed species, collecting sites, and vegetation periods, in line with the conclusions of other studies at laboratory or greenhouse scale (Soudek et al. 2004, 2007; Tykva and Podracká 2005). The specific ^{226}Ra activities of the roots were considerably higher than the aboveground parts confirming the root tropism of this radioisotope. *M. piperita* was found to be highly effective in phytoremediation, especially by the end of the vegetation period.

With the same purpose, gross $\alpha + \beta$, ^{226}Ra, and ^{137}Cs in soils and medicinal plants growing spontaneously in the Crucea and Leşu Ursului mining areas were monitored from 2004 to 2008 (Costin et al. 2010). ^{137}Cs was accidentally found in a soil sample collected in a place uncovered with vegetation in the Leşu Ursului region (Tănase et al. 2009; Costin et al. 2010; Popa et al. 2010). Its origin is obviously the Chernobyl accident. All plant species had shown similar capabilities for gross $\alpha + \beta$ and ^{226}Ra accumulation. The soil-to-plant transfer coefficients are of about 1–2, in line with values already reported and lower than ones found for other much effective species such as *M. piperita*, *F. vesca*, or *Abies alba* (Petrescu and Bilal 2003; Popa et al. 2008a). The statistical studies show no interdependence between the collecting places at a given time and the activity (gross $\alpha + \beta$ and ^{226}Ra, respectively). All tested statistical models were conducted to very low values of the determination coefficients, which made senseless to apply any regression model as a function of the collecting time (Costin et al. 2010).

3 Wheat Germination: A Simple Model Study for Radioactive Site Remediation; Toxicological and Biochemical Aspects

The literature contains a number of studies dealing with the uptake of natural and anthropogenic radionuclides on wheat as main component of the food chain (Aarkrog 1969; Eisenbud 1973). Thus, ^{137}Cs and ^{90}Sr released into the environment may enter the food chain from plants to human and pose health potential risk (Gouthu et al. 1997).

Thus, the uptake of naturally occurring isotopes ^{238}U, ^{232}Th, ^{226}Ra, and ^{40}K by wheat was studied under natural field conditions (Pulhani et al. 2005). Transfer factors ranged from 10^{-4} for ^{238}U to 3.1 for ^{40}K. Most of the uranium, thorium, and radium (54–75 %) were retained in roots, while 57 % of potassium was accumulated in shoots. Similar conclusions were derived by Lindahl et al. (2011), which studied the distribution of natural radionuclides in organically and conventionally grown wheat. Thus, most of thorium and radium were found in the root and steam, while potassium showed the highest activity concentration in the steam and lowest in the root.

Also, the uptake of several anthropogenic radionuclides from different soils in wheat was extensively studied (Djingova et al. 2005; Yamaguchi et al. 2007). The ^{137}Cs content of *Triticum durum* collected throughout Italy after the Chernobyl accident has been measured (Lotfi et al. 1990). The transfer factor of ^{137}Cs from soil to wheat straw range from 22 to 68, while the ratio of ^{90}Sr in what grain to exchangeable ^{90}Sr concentration in soil was in the range of 0.05 and 0.2. Accumulation of ^{134}Cs and ^{85}Sr on different parts of *Brassica napus* L. (oilseed rape) and *Triticum aestivum* L. (wheat) was reported by Bengtsson et al. (2012, 2013). The highest transfer in wheat grains was found for ^{85}Sr during at a growth stage close to the harvest. Most important, it was concluded that the highest risk for transfer of the radioactivity into humans via the food chain occurred by the end of the growing period—in line with our in-field observations (Popa et al. 2008a).

Last but not least, translocation of ^{125}I, ^{75}Se, and ^{36}Cl in edible parts of wheat, following wet foliar contamination under field conditions, was recently reported by Hutervent et al. (2013). Very high transfer factors were obtained for all studied radioisotopes. However, while chlorine was very mobile and quickly diffuses through the plant, iodine was preferentially in or on the leaves.

In 2007, our group proposed for the first time the wheat germination as a simple model test for radioactive site remediation, in order to understand toxicological, biological, and biochemical mechanisms that make phytoremediation work (Popa et al. 2007). A dose-response assay includes seed germination and analysis of shoot and root elongation on paper. Analyses of plant responses to the radioactivity or the tolerance level of some seeds or plantlets to a given radionuclide were based on various bioassays as those described in the literature (Weiss et al. 2006).

Wheat germination studies in the presence of stable or radioactive cesium, cobalt, and mercury were conducted and previously reported (Popa et al. 2007, 2008b; Murariu et al. 2009). Later on, uranyl uptake from solutions of different concentrations was also studied. The preparation of the samples, sampling procedure, instrumental setup, and the retention degree calculation were conducted as previously described (Popa et al. 2006). The radioactivity measurements are carried out by spectrometry for the γ-emitting ^{203}Hg, ^{137}Cs, and ^{60}Co, respectively, by fluorimetry in the uranyl case. Tukey's test (Snedecor 1940) was used to process all data within the germination experiment. Besides, the standard deviation (s_x), t and k parameters were calculated in order to detect a statistically significant effect, if any.

The noxious effect of mercury ions (Patrick 2002) on wheat germination and seedling growth was studied as a function of the inorganic mercury form (stable or radioactive) as well as a function of concentration (Popa et al. 2007). A typical example of wheat germination test is presented in Fig. 1, in which the wheat seeds germinated during one week following the treatment with water, 10^{-2} M cysteine (Cys–S–S–Cys) solution, 10^{-3} M ^{203}HgCl$_2$ solution, and a solution containing 10^{-3} M ^{203}HgCl$_2$ and 10^{-2} M cystine, respectively. When compared with the

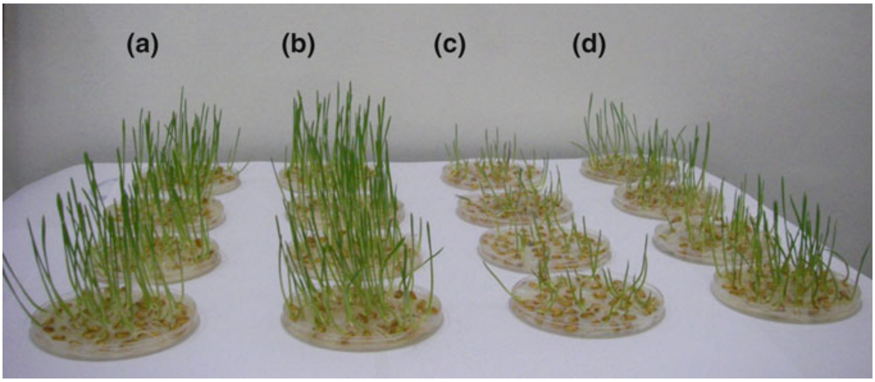

Fig. 1 Effect of $^{203}HgCl_2$ on wheat germination: treatment with water (**a**), 10^{-2} M cysteine solution (**b**), 10^{-3} M $^{203}HgCl_2$ solution (**c**), and a solution containing 10^{-3} M $^{203}HgCl_2$ and 10^{-2} M cysteine (**d**)

Table 1 Distribution of the studied cations (stable and radioactive forms) in the stems and roots of seven-day seedlings experiments

Ion	Concentration in molar	Germination rate in %	Plantlets in lot	Root weight, in g	Weight of the stems and leaves, in g	Total height of the shoots in cm
Hg^{2+} (stable)	10^{-3}	94	46	1.73	1.93	313
$^{203}Hg^{2+}$	10^{-3}	89	39	1.21	1.56	249
Cs^{+} (stable)	10^{-3}	95	46	1.48	1.86	231
$^{137}Cs^{+}$	10^{-3}	80	35	0.19	0.29	73
Co^{2+} (stable)	10^{-3}	94	44	0.74	1.58	243
$^{60}Co^{2+}$	10^{-3}	84	39	0.43	0.97	179
UO_2^{2+}	5×10^{-3}	89	42	1.67	1.91	342
UO_2^{2+}	10^{-3}	90	43	1.76	2.09	356
UO_2^{2+}	5×10^{-4}	93	44	1.81	2.14	374
UO_2^{2+}	10^{-4}	95	45	1.93	2.33	400

stable mercury at similar concentrations, the ^{203}Hg was more hazardous to the seeds and seedlings. Part of the seeds germinated but failed to grow in the presence of both radioactive and stable mercury.

Germination rates, number of plantlets in lot (out of 50), root weight, weight of the aerial part, and total height of the shoots after seven-day seedling experiments in the presence of active and stable mercury, cesium, and cobalt, as well as uranyl, are summarized in Table 1. More details on chemicals and instrumental setup, as well as statistical interpretation may be found in Popa et al. (2007, 2008b) and Murariu et al. (2009). In the uranium case, the fluorimetric determination of the uranyl ion has been used (Popa 2013).

The radioactive chloride solutions of 10^{-3} M $^{203}Hg^{2+}$, $^{137}Cs^{+}$, and $^{60}Co^{2+}$ as well as the stable Hg^{2+} show an inhibitory effect on the wheat germination. From these data, it became evident that the mercury has shown the most toxic effect, followed by cesium, which is very radiotoxic. It was proved that stable mercury chloride solutions show highly inhibitory activity on the wheat germination, while the same concentrations of $^{203}Hg^{2+}$ ions are even more (radio)toxic. Part of the seeds germinated but failed to grow in the presence of both radioactive and stable mercury.

Since the activities of the solutions of γ-emitting radioisotopes were approximately equals (350 ± 25 MBq ml^{-1} at the beginning of the experiments), it became clear that the germination and the growing rate are not influenced by the gamma energies emitted by the tested radioisotopes. Moreover, the uranyl concentration does not influence drastically the germination rate (ranging from 10^{-4} to 5×10^{-3} M), the weight, and length of the biological product of the seeding experiment. This may conduct to the conclusion that the uranyl ion is not retained by the wheat during the germination, but further studies are to be conducted into this direction.

Although mercury accumulation was higher in roots, a significant amount of this element accumulated in the aerial parts. Our results are in agreement with other findings (Cavallini et al. 1999), which show that the root is an important absorption site for mercury and creates a barrier to further transport of this element to the upper part of the plant.

According to Hosseinimehr (2007), the ideal radioprotective agent must have (1) significant protection against the effect of radiation; (2) general protective effect on the majority of organs; (3) acceptable route of administration; (4) acceptable toxicity profile and protective time-window effect; (5) acceptable stability profile; and (6) compatibility with the wide range of other drugs that will be available to patients or personnel (then dealing with radiotherapy). Several radioprotective agents (glutathione, cysteine, cysteine, or even synthetic thiol peptides) were used in our experiments.

Within germination experiments, wheat seeds proved their sensitivity to the γ-emitting radioisotopes of mercury, cesium, and cobalt, whereas cysteine had an antiradiotoxic effect (especially in the case of cesium). Germination rate was significantly reduced in the case of the treatment with 10^{-3} M solution of $HgCl_2$ as compared to the control, while all the radioactive solutions drastically reduced the germination rate. The addition of cysteine to radioactive cesium and cobalt or to both forms of mercury resulted in the increasing the number of germinated seeds. In addition, stable cesium and cobalt displayed a stimulatory effect on wheat germination, although the differences between the blank with H_2O and Cs^{+}/Co^{2+} were not statistically significant. While cysteine cannot react with mercury ions due to its disulfide bridge, it protected tissues from the radioactive damage probably by capturing the newly generated radicals. In order to compare these results with the one obtained using a classical radioprotective agent, glutathione had been used in identical working conditions. A powerful detoxification action of

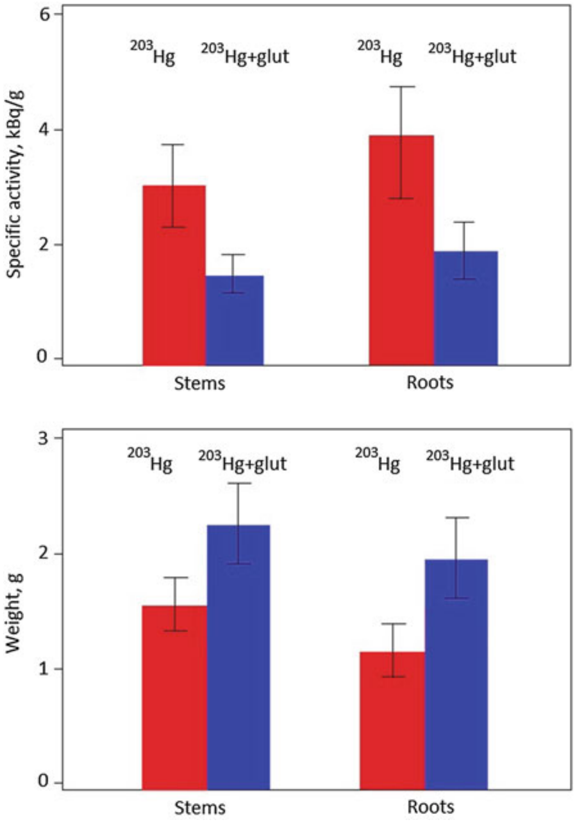

Fig. 2 Distribution of radiomercury in the stems and roots of the wheat after 7-days seedlings experiment in the presence and the absence of the glutathione (*up*). Weight of stems and roots of the wheat after 7-days seedlings experiment in the presence and the absence of the glutathione (*down*)

glutathione against mercury and, especially, its radioactive form was proved (Fig. 2).

The thin-layer radiochromatography data indicated that the sugars are most important fraction in respect with mercury accumulation (Fig. 3). From those data, we can only suppose that the phenomenon is related with the excellent coordination properties of the sugars toward the considered cations. Since a part of the radioactive ions were not extracted, it might be that it was associated with some other (bio)chemical fractions presented in plantlets, but not separated by the method we used (e.g., proteins, inorganic salts).

Under extremely adverse conditions of radium and uranium contamination, compensatory processes, resulting in animal and plant survival, were observed (Geras'kin et al. 2007). However, no signs of adaptation were detected. The findings suggest that adverse somatic and genetic effects are possible in plants at

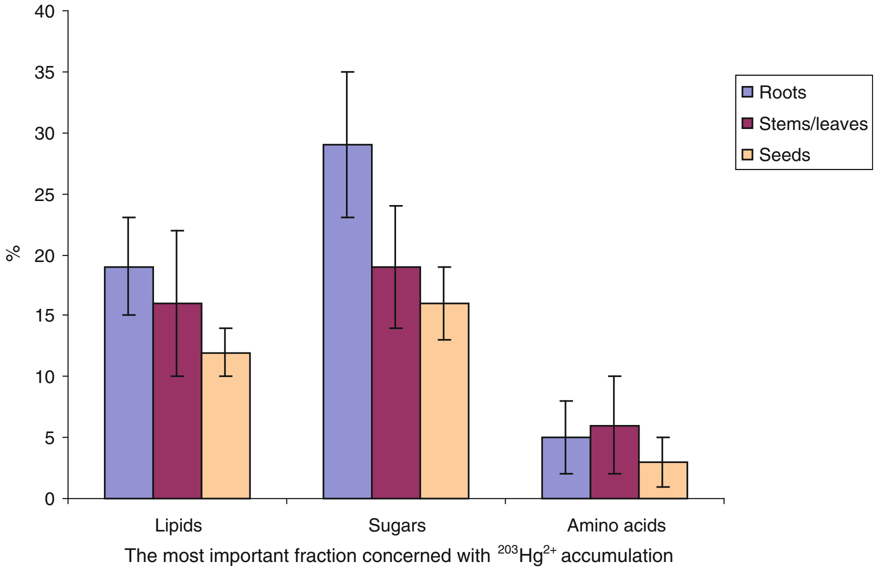

Fig. 3 The amount of mercury retained in several biochemical fractions extracted from germinated wheat, expressed as percent of total accumulated mercury (isotope dilution experiments followed by thin-layer radiochromatographic technique, developed by Cecal et al. (2002a, c, d)

sites with an enhanced level of natural radioactivity. Thus, natural radioactivity seems to stimulate the growth processes, photosynthesis, endogenous low molecular weight antioxidant synthesis, as well as adaptive response.

The use of yeast suspensions in the decontamination of radioactive residual waste waters was studied by many authors (Gok et al. 2011; Selvakumar et al. 2011; Liu et al. 2013; Piccirillo et al. 2013; Wang and Liu 2013). Interestingly, some of them highlighted the biological impact of radionuclides (Humelnicu et al. 2004) and suggest that yeast organisms protected theirselves against radiotoxic influence of low amounts of uranyl ions, whereas higher concentrations of thorium ions penetrated the protection system. Such data are concordant with the assertion that living organisms, including plant ones, react against the radiotoxic action of the radionuclides (Geras'kin et al. 2013), as a function of their vitality. When their capability of reaction is over passed, then the radioactive elements may enter into the cell and damage it. Moreover, the concentration of free amino acids in living cells seems to be a function of the stress intensity; low concentrations of uranyl and thorium ions induce a decrease in amino acid level in yeast cells, suggesting an increased protein synthesis, whereas the high concentrations of radioactive ions will increase the free amino acid content. In fact, the biostructure of living cell is damaged by the radioactive ions, which behave as unspecific stressors (Drochioiu 2006).

It was also shown that the cesium and manganese uptake in rye, oats, barley, and wheat is higher than that of strontium and cerium (Aarkrog 1969). Besides, strontium was eliminated from plants in about 3 weeks, whereas cesium was much longer retained in plants. This suggests that plants pose defending mechanisms, other than deposition of the toxic ions in vacuoles. Plant organisms retain some metal ions such as potassium and calcium. Cesium may easily replace potassium in the cell biostructure (Drochioiu 2006), and thus, the retention of cesium is understandable.

Ohmori et al. (2014) demonstrated that high nitrogen and low potassium in soil concentrate radiocesium both in straw and rice seeds. These findings have been expected since potassium may be easily replaced by cesium under normal physiological conditions, and nitrogen adsorbed by plants is transformed into proteins able to bind alkaline ions. Since cesium is a congener of potassium, living cells are able to take up cesium using the potassium transporters (Okuda et al. 2013).

4 Conclusions and Perspectives

The present chapter summarized our previous contributions on the uptake of radionuclides in laboratory, greenhouse, or in-field conditions. Radionuclides are considered as major environmental pollutants, being cytotoxic, mutagenic, and carcinogenic. The chelating processes may increase their uptake by plants. The newly proposed wheat germination experiment was used to assess the biological and biochemical mechanisms involved in radionuclide remediation through plants. In order to select the best phytoremediation conditions, the effects of radioactive ions on the plant physiology were extensively studied. Thus, their accumulations in different parts of plant organisms were highlighted. The effect of several radioprotective agents was also considered; those experiments may represent the first step for further in vivo studies of heavy metal or radioactive ions incorporation. Further research is needed for thoroughly understanding the role of cysteine as well as of the cysteine peptides as protectors against radioactive ions and free radicals produced in living organisms. As a part of the non-intervention approach in the environmental radioactive remediation, phytoremediation may play a very important role. Evaluation of the potential of agricultural and spontaneous plants to accumulate radioactive compounds is important for the containment of any released pollutants, the prevention of such from endangering natural ecosystems and nearby human populations, and the development of phytoremedial strategies. The uptake mechanisms are very diverse, as a function of plant developing stage (vegetation period), radioisotope concerned, physical and chemical characteristics of the concerned system, the presence of competing ions, etc. Thus, every system must be regarded with independently special concern. Moreover, data collected at laboratory scale may be seriously influenced by the environmental conditions than moving to the field.

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Transfer of Radionuclides to Plants: Influence on the Speciation of Radionuclides in Soil

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Abstract The quantification of the soil-to-plant transfer by means of transfer factor or concentration ratios values presents high range of variation, about 4–5 orders of magnitude for radiocesium. This range can be partially explained by the different association of radionuclides to soil particles, which can be assessed by speciation procedures. The fact that there are a lot of speciation procedures in the literature may, in some occasions, make its interpretation difficult. The source of radionuclides is a major factor influencing the speciation. The anthropogenic radionuclides associated with fuel particles present usually low mobility, although they can be weathered with time. Regarding the radionuclides released in the global fallout, the ^{90}Sr is the most bioavailable. Plutonium is usually associated with organic matter. The mobility and bioavailability of radiocesium depends on the soil clay content, and is also time dependent. The naturally occurring radionuclides in soil are mainly associated with fractions strongly fixed, because they mainly occur in minerals forming part of soil particles. The speciation of soil can also be modified by agricultural procedures, such as the addition of fertilizers or phosphogypsum. The fertilization can be used to reduce the soil-to-plant transfer of radiocesium and radiostrontium by supplying stable elements, potassium, and calcium, respectively, so that their content in soil solution decreased. The phosphate-based fertilizers have also naturally occurring radionuclides, which can be transferred to plants. Phosphogypsum, which can contain high levels of radium, is used as soil amendment. However, its radium content is mainly associated with immobile fractions, and its transfer to plants is of the same order of magnitude than without phosphogypsum amendment.

Keywords Transfer · Speciation · Bioavailability · Anthropogenic radionuclides · Naturally occurring radionuclides

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Contents

1 Introduction

As consequence of the atom bomb blasts during World War II, anthropogenic radionuclides were first released into the environment. Later, during the 1950s and 1960s, there were a great number of atmospheric nuclear weapons tests, which released huge amounts of radionuclides into the atmosphere. Due to atmospheric circulation, they became distributed worldwide and were ultimately deposited onto the soil (UNSCEAR 2000). Once they were on the surface of soil, they began to interact with the different soil components by different processes, and also to migrate downwards as consequence of weathering and percolation. These processes depended on the chemical properties of the radionuclide, the physicochemical properties of the soil on which they were deposited, climate, latitude, among others. As result, the radionuclides were associated with different degrees to soil particles, and partially able to be transferred to plants, and from them to animals and humans.

Naturally occurring radionuclides are also present in the environment, mainly associated with different minerals, and forming part of soil particles. Uranium, thorium, their descendants in the natural decay series, and ^{40}K are such radionuclides. As they are present in the soil, they also are susceptible to be transferred to plants and enter the food chain. The concentration of these naturally occurring radionuclides in the soil depends mainly on geological reasons. There are minerals with high content of these radionuclides, which serve as raw materials for industrial processes. These industries are usually denominated naturally occurring radioactive material (NORM) industries. The production of fertilizers from phosphate rock, coal-fired power plants, and oil and gas extractions are some examples of NORM industries (IAEA 2003). There are other naturally occurring radionuclides of cosmogenic origin, such as ^{7}Be, and ^{22}Na, but their transfer to plants is more limited.

Table 1 Range of soil-to-plant transfer factors for radiocesium for different types of plants

Plant group	Plant compartment	Range TF
Cereals	Grain	2.0×10^{-4}–0.90
	Stems and shoots	2.8×10^{-3}–3.7
Leafy vegetables	Leaves	3.0×10^{-4}–0.98
Non-leafy vegetables	Fruits, heads, berries, buds	7.0×10^{-4}–0.98
Leguminous vegetables	Seeds and pods	1.0×10^{-3}–0.71
Root crops	Roots	1.0×10^{-3}–0.88
	Leaves	6.0×10^{-3}–0.45
Tubers	Tubers	3.7×10^{-3}–0.60
Grass	Stem and shoots	4.8×10^{-3}–0.99
Leguminous fodder	Stem and shoots	0.01–1.8
Pasture	Stem and shoots	0.001–5.0
Herbs	Stems and leaves	4.8×10^{-3}–2.8
Other crops	All	3.6×10^{-2}–2.2

Data from (Nisbet and Shaw 1994; Wang et al. 1998; Tsukada and Nakamura 1999; Copplestone et al. 2001; IAEA 2010; Barnett et al. 2013)

2 Quantification of Radionuclide Transfer to Plants

The first approach to quantify the transfer of radionuclides to plants is based on the so-called transfer factors, TF, transfer coefficients, TC, or concentration ratios, CR, which are usually defined as the ratio between the radionuclide content in plant and the radionuclide content in soil (see Eq. 1). Other way of quantification, the aggregated transfer factors, TF_{agg}, has also been used when a nuclear accident occurred. The TF_{agg} can be defined as the ratio between the radionuclide content in plant and the radionuclide deposition on soil (see Eq. 2).

$$\text{TC, TF, CR} = \frac{\text{Bq kg}^{-1}\ \text{f.w. in plant}}{\text{Bq kg}^{-1}\ \text{d.w. in soil}} \tag{1}$$

$$\text{TF}_{agg} = \frac{\text{Bq kg}^{-1}\ \text{f.w. in plant}}{\text{Bq/m}^2\ \text{in soil}} \tag{2}$$

Radiocesium is the long-lived anthropogenic radionuclide most widely studied, because its release was the highest due to global fallout and other nuclear accidents (UNSCEAR 2000). Table 1 shows the range of *TF* values reported in the literature for radiocesium to different plant groups worldwide. These values varied within five orders of magnitude, which suggested that it is affected by many variables, such as the type of soil in which they were grown (Nisbet and Shaw 1994; IAEA 2010) and the kind of plant considered (Nisbet and Shaw 1994; Korobova et al. 1998; IAEA 2010). It can also be observed that the radiocesium transfer to different biological compartments presented variations. The maximum value of transfer to stems and shoots was higher than to grain for cereals. It also occurred for root crops, in which the transfer to root was higher than to leaves. The

Table 2 Range of soil-to-plant transfer for different anthropogenic and naturally occurring radionuclides for grass as an example of RAP

Radionuclide	Range TF	Radionuclide	Range TF
Am	4.2×10^{-4}–0.26	Ra	3.6×10^{-4}–1.6
Cs	4.8×10^{-3}–0.99	Pb	0.11–1.0
Sr	0.25–2.8	Th	7.4×10^{-4}–0.65
Pu	5.0×10^{-5}–2.7×10^{-4}	U	2.0×10^{-4}–5.5

Data from (IAEA 2010; Barnett et al. 2013)

radiocesium transfer also depended on the nutrients available in the soil and the nutritional requirements of each plant. The TF_{agg} values varied within the range 0.0006–0.47 $m^2\ kg^{-1}$ (Drissner et al. 1998; Strandberg 1994; Bunzl et al. 1999; Fesenko et al. 2001), which showed a variation of about four orders of magnitude.

However, there are other anthropogenic and naturally occurring radionuclides that are in the environment and able to be up taken by plants. Table 2 shows their range of variation for grass, as an example of reference animal and plant (RAP) (ICRP 2009). The different chemical properties of radionuclides also influenced their transfer from soil to plant, depending on the nutritional requirements. The soil-to-plant transfer to plant decreased in the following order:

$$\mathrm{Sr,\ U,\ Ra,\ Pb} > \mathrm{Cs} > \mathrm{Th} > \mathrm{Am} \gg \mathrm{Pu}$$

The quantification of the process of radionuclide transfer from soil to plant using these transfer factors has some limitations. This approach assumes that the transfer process is steady, without any changes with time, which can be assumed for boreal ecosystems. However, in Mediterranean ecosystems, in which dry and wet seasons alternate, the transfer of radionuclides showed a seasonal dependence reflecting the availability of nutrients (Baeza et al. 2001; Schuller et al. 2005). Another problem with these definitions is the concept of the radionuclide content of soil. It is not well specified, and it can raise some doubts about the depth to be considered: surface soil (0–5 cm), the layer of soil in which roots are located, etc.

In these definitions, the total fraction of radionuclides in soil is usually considered. But, once the radionuclides were deposited on soil, they began to react with soil particles and a process of immobilization occurred, depending on the physicochemical properties of radionuclides and soil, and the chemical form in which they were released into the environment. Therefore, not all radionuclides, but a fraction of them, would be able to be transferred to plant.

3 Speciation Schemes of Radionuclides in Soil

The association of radionuclides to soil particles is usually assessed by the use of speciation schemes or sequential extraction procedures. They can be classified as either methods based on a sequential extraction of soil with selective reagents or those in which the soil is sequentially treated with chemical solutions of increasing replacement/dissolving power (Alexakhin and Krouglov 2001). One of the major disadvantages of this technique is that there is no unified procedure to carry out. In the literature, there are a great variety of procedures, many of them with similar reagents and/or concentrations, but used in different order. Table 3 shows the reagents and steps used in different speciation schemes reported in the literature. Most of them are based on that proposed by Tessier et al. (1979) for metal speciation. As it can be observed in Table 3, there is a great variation on the number of steps and reagents involved in each speciation scheme.

The use of speciation schemes gives extremely useful information about the association of radionuclides to the different components of the soil. However, one of its major problems is the interpretation of the data obtained. Although the reagents are usually designed to attack a single geochemical phase, they are not completely specific (Schultz et al. 1998). The use of denominations for some fractions can sometime be confusing or misleading. This can lead to the fact that the application of different speciation schemes in soils gave different results (Blanco et al. 2004).

The soil solution is one of the easiest fractions to extract in speciation schemes. It consists of water present within pores between soil particles, which contain a great variety of chemical compounds, colloids, and suspended particles. Therefore, it is considered to be an important medium for the transfer of radionuclides and nutrients from soil to plants. The extraction of soil solution from the soil can be carried out by different techniques: using porous ceramic cup samplers (Nisbet et al. 1993a), by addition of distilled water and subsequent centrifugation (Agapkina and Tikhomirov 1994; Agapkina et al. 1995; Amano et al. 1999), or by use of a disk impregnated with a specific resin in direct contact with the soil (Jouve et al. 1999). As one method for its extraction is the water addition, the soil solution can be expected to be similar to the water-soluble fraction defined in some sequential speciation procedures. The association of radionuclides to different compounds detected in soil solution has also been reported. Size and charge fractionation techniques are used to separate the chemical species present according to their nominal molecular mass. High-molecular weight (HMW) fraction (MW $>$ 10 kDa) consist of nanoparticles, colloids, polymers, pseudo-colloids, etc., which are assumed to be mobile in water due to mutual repulsion and Brownian movement. Low-molecular weight (LMW) fraction (MW $<$ 10 kDa, and Ø $<$ 1 nm) consist of single compounds, inorganic and organic ions, complexes, molecules, etc. The LMW species are considered to be mobile and potentially bioavailable depending on their charge properties and lipophilic characteristics. Radiostrontium and radiocesium were mainly associated with the LMW fraction, although in different ranges, ^{90}Sr in the fraction about 400 Da and ^{137}Cs in the 800–1,100 Da (Nisbet et al. 1993a; Agapkina and Tikhomirov 1994; Agapkina et al. 1995; Amano et al. 1999). Plutonium and americium were present mainly in the HMW fraction (Agapkina et al. 1995). The content of each radionuclide in the soil solution was not the same, and decreased in the following order: $^{90}\text{Sr} > {}^{137}\text{Cs} > {}^{239,240}\text{Pu} \geq {}^{241}\text{Am}$ (Agapkina et al. 1995).

Table 3 Summary of different steps in several sequential extraction procedures in the literature

Speciation steps							References
H_2O	NH_4AcO 1 M	NaAc (HAc)	$NH_2OH{\cdot}HCl$ 1 M + NH_4Ox	H_2O_2 + NH_4AcO	Residual	–	Tessier et al. (1979)
H_2O	NH_4OAc 1 M	H_2O_2 + NH_4AcO + HNO_3	HNO_3 7 M	Residual	–	–	Fawaris and Johanson (1995)
H_2O	NH_4AcO 1 M	HCl 1 M	HCl 6 M	Residual	–	–	Pavlotskaya (1974)
$CaCl_2$ 0.05 M	HAc 0.5 M	$Na_4P_2O_7$ 0.1 M	HOx 0.1 M + NaOx 0.175 M	Residual	–	–	Cook et al. (1984)
H_2O	$MgCl_2$ 0.4 M	NH_4AcO	$NH_2OH{\cdot}HCl$ (HAc)	H_2O_2 + HNO_3	HNO_3 8 M	Residual	Schultz et al. (1998)
NH_4AcO 1 M	$NH_2OH{\cdot}HCl$ 0.04 M	H_2O_2 + NH_4AcO + HNO_3	HNO_3 7 M	Residual	–	–	Riise et al. (1990)

AcO = acetate. Ox = oxalate

In some schemes, the water-soluble fraction can be omitted because it may be considered that the following fraction, usually exchangeable, is also able to extract the radionuclides associated with the water-soluble fraction. The radionuclide content of the exchangeable fraction is associated with ionic exchange sites in soil, which are supposed to the readily available. The extractants frequently used for this fraction are NH_4AcO, $MgCl_2$, $CaCl_2$, EDTA, DTPA, NH_4NO_3, KCl, or $NaNO_3$ (Kennedy et al. 1997; Komosa 2002; Rigol et al. 2002). The K^+ and NH_4^+ ions are considered to be competitive with Cs^+ in soils, and therefore able to desorb them effectively. The NH_4OAc 1 M at pH 7 is considered to be a robust extractant for acidic or neutral soils but unsuitable for alkaline soils (Kennedy et al. 1997). However, it can be buffered into the soil pH to extend the range of pH in which it can be used. In aquatic sediments, it has the drawback that may also attack the carbonates present. $MgCl_2$ 1 M at pH 7 was found to extract less carbonates than NH_4AcO (Kennedy et al. 1997). Divalent ions are also able to desorb Cs^+ from nonspecific sites, but are considered to be less effective in desorbing Cs^+ from clay interlayers (Rigol et al. 2002).

In the Tessier scheme (Tessier et al. 1979), there are also other fractions considered. The carbonated fraction can be extracted with sodium acetate in acetic acid (Tessier et al. 1979). The reducible fraction, also named in some procedures bound to Fe and Mn oxides, are obtained by the application of a reducing extractant, generally $NH_2OH \cdot HCl$ (Tessier et al. 1979; Riise et al. 1990; Schultz et al. 1998; Komosa 2002).

The association of radionuclides with organic matter present in the soil can be assessed by using different reagents. The oxidable organic matter is usually extracted with H_2SO_4, H_2O_2, and NaClO (Tessier et al. 1979; Riise et al. 1990; Fawaris and Johanson 1995). The hydrolysis with H_2SO_4 can break down the cellulose and hemicellulose complexes present in the soil. The NaClO was able to extract more radiocesium than H_2O_2, and it was also observed that the soil minerals were less destructed (Vinichuk et al. 2005). On the other hand, the organic acids present in soil, mainly humic and fulvic acids, can be extracted using $Na_4P_2O_7$ and NaOH (Kononova 1982; Lee and Lee 2000). These reagents are able to precipitate or form soluble complexes with Ca, Fe, Al, and other polyvalent cations to which humic substances are bound (Kononova 1982). Humic and fulvic acids are extracted together, and they can be separated by adjusting the solution pH to 2. Humic acids precipitate while fulvic acids remain soluble (Lee et al. 2000). Organic extractants can also be used to extract radionuclides from humic and fulvic acids present in soils, such as trimethylchlorosilane and triethylchlorosilane in the presence of dimethylformamide (Szabo et al. 1991). It was based on the modification of the solubility of humic substances by the silylation of the carboxylic, phenolic, alcoholic, and amino moieties of humic and fulvic acids (Szabo et al. 1991).

Some speciation schemes use inorganic acids in advanced steps. The use of dilute inorganic acids, as HCl 1 M, can remove cations from exchange complexes in the soil, and also dissolve oxides, hydroxides, carbonates, and some alkaline earth compounds. This fraction can be considered as potentially available, whereas

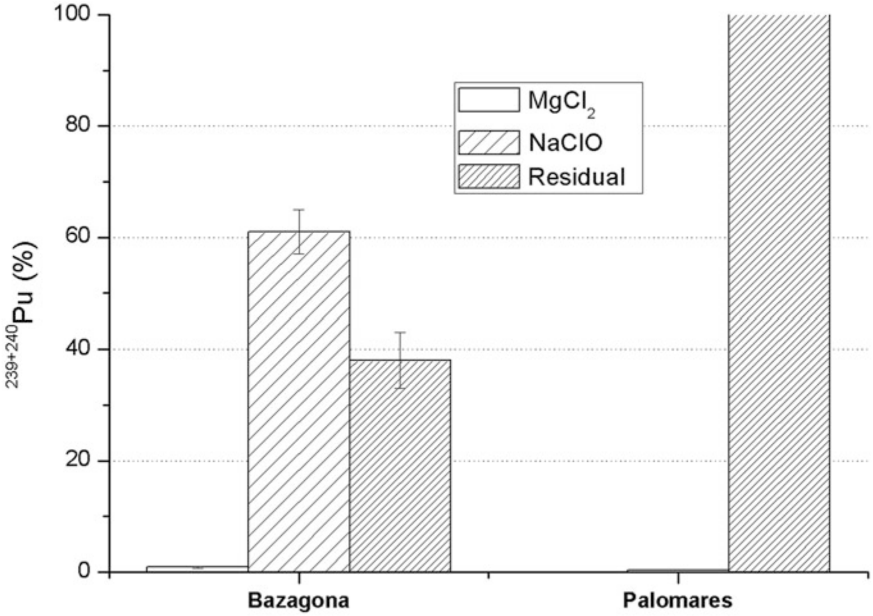

Fig. 1 Speciation of $^{239+240}$Pu in two ecosystems affected by different contamination events: global fallout and Palomares accident. The fractions considered were exchangeable, extracted with $MgCl_2$, associated with organic matter, extracted with NaClO, and residual. Data from Baeza et al. (2004)

the use of concentrated mineral acids (HCl 6 M, HNO_3 7 M or 8 M) are able to extract cations from interlayer or structural positions not readily accessed by exchange reactions (Krouglov et al. 1998). Finally, the residual fraction represents the radionuclides strongly attached to soil particles, which have the lowest probability to be available.

4 Factors Affecting the Speciation of Radionuclides in Soil

The speciation of radionuclides in soil can be influenced by different factors, such as the chemical form and time elapsed since the deposition occurred, the physicochemical properties of soil, its clay and organic matter content, the climate, etc. The chemical form in which the radionuclides were deposited is of crucial importance for their speciation. If the anthropogenic radionuclides released were associated with refractory particles of fuel, its presence in more mobile and bioavailable fractions is expected to be limited. As a way of example, in Fig. 1 shows the speciation of $^{239+240}$Pu in the fractions exchangeable, extracted with $MgCl_2$, associated with organic matter, extracted with NaClO, and residual in two ecosystems affected by different fallout: global fallout and Palomares accident in 1966. The $^{239+240}Pu$ in Palomares ecosystem was almost exclusively associated with the residual fraction; while in the ecosystem affected by global fallout it was mainly associated with the organic matter fraction followed by residual and exchangeable (Baeza et al. 2004). The association of plutonium with organic matter has also been reported by other authors using other reagents, $Na_4P_2O_7$ and oxalic acid/ammonium oxalate, and H_2O_2 (Cook et al. 1984; Komosa 2002). The humic substances in soils, mainly composed of organic acids, were also able to bound plutonium and americium efficiently (Amano et al. 1999; Lee and Lee 2000). The plutonium associated with humic acids was greater than that associated with fulvic acids (Lee and Lee 2000).

Figure 2 shows the speciation of anthropogenic (^{137}Cs, ^{90}Sr, $^{239+240}Pu$, ^{241}Am) and naturally occurring radionuclides (^{40}K, ^{238}U, ^{226}Ra, ^{210}Po, ^{232}Th) in an ecosystem whose source term was mainly global fallout. The scheme used was a modification of that of Pavlotskaya (1974). The fractions considered was exchangeable (extracted with NH_4AcO), diluted acid (extracted with HCl 1 M), concentrated acid (extracted with HCl 6 M), and residual. The distribution pattern for anthropogenic and naturally occurring radionuclides was different. The latter were mainly associated with the residual fraction, as consequence of forming part of minerals in soil particles. Only ^{210}Po, presented values higher than 20 % in the diluted-acid and concentrated-acid fractions. The distribution pattern of anthropogenic radionuclides depended on which one was considered. The ^{90}Sr was mainly associated with the exchangeable fraction followed by diluted- and concentrated-acid fractions and residual. The association of radiostrontium with exchangeable fraction, which is usually considered as mobile and able to be transferred to plants, can explain its greater downward migration in soils than other anthropogenic radionuclides (Kagan and Kadatsky 1996; Forsberg et al. 2000). In areas close to Chernobyl Nuclear Power Plant (NPP), ^{90}Sr was observed to be associated with fuel particles, thus being associated with acid-digestible and residual fractions (Krouglov et al. 1998). However, the weathering of the fuel particles released ^{90}Sr into the environment, depending on the soil acidity, and was observed an increase of the exchangeable fraction (Krouglov et al. 1998).

The ^{137}Cs was mainly associated with concentrated-acid and residual fractions, being the exchangeable fraction lower than that of ^{90}Sr. This distribution pattern was also observed in other ecosystems (Riise et al. 1990; Forsberg et al. 2001). The radiocesium associated with exchangeable fraction (extracted with NH_4OAc) in soils was found to be within the range 1.8–29 % of the total content of soil (Riise et al. 1990; Bunzl et al. 1997; Lee and Lee 2000; Forsberg et al. 2001; Vinichuk et al. 2005). The exchangeable fraction was observed to decrease while increasing the lapsus of time since the deposition of radiocesium occurred (Cheshire and Shand 1991; Krouglov et al. 1998; Baeza et al. 1999; Forsberg et al. 2001). This is usually known as aging effect, and is associated with the irreversible sorption of cesium in clay at frayed edge sites (FES). The selective adsorption of FES can be attributed to the small hydratation energy of cesium ions. The energy for desorption was found to be so large that desorption was energetically unfavorable (Stauton et al. 2002).

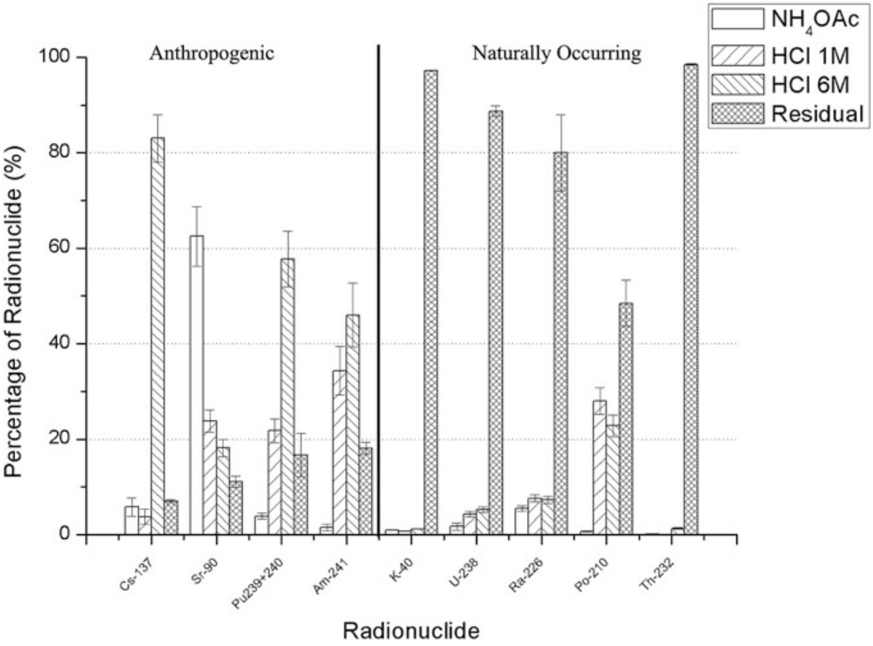

Fig. 2 Speciation of anthropogenic (^{137}Cs, ^{90}Sr, $^{239+240}$Pu, ^{241}Am) and naturally occurring radionuclides (^{40}K, ^{238}U, ^{226}Ra, ^{210}Po, ^{232}Th) in an ecosystem mainly influences by global fallout. Data from Baeza et al. (2005), Baeza and Guillén (2006a), Baeza et al. (2006b), Guillén et al. (2009)

The FES selectiveness for monovalent cations decrease in the order: $Cs^+ > NH_4^+ > Rb^+ > K^+ > Na^+ > Li^+$ (Rigol et al. 2002; Stauton et al. 2002). The K^+ content in soil can cause the collapse of the expanded interlayers, tapping the cesium binded inside (Rigol et al. 2002).

The distribution pattern of plutonium and americium in this soil (Fig. 2) was similar. They were mainly associated with the concentrated-acid fraction, followed by diluted-acid, residual and exchangeable fractions.

5 Bioavailability of Radionuclides

The data obtained from the speciation schemes can be used to analyze the soil-to-plant transfer of radionuclides. The bioavailable fraction of radionuclides in soil may be defined as the fraction of them able to be transferred to plants. Positive correlations between the transfer factor and bioavailable fraction have been observed for radiocesium (Fesenko et al. 2001). The water soluble and exchangeable fractions are usually considered to be very mobile in soil and, therefore, readily available to be transferred. Other approach is to consider that only the fractions not strongly attached to soil particles would be able to be transferred. The diluted-acid fraction would be included in the latter, as it is considered potentially available or mobile (Fesenko et al. 2001; Baeza et al. 2006). The diluted-acid fraction (HCl 1 M) is able to dissolve oxides, hydroxides, carbonates, and some alkaline earth compounds present in the soil. The carbonated fraction in the Tessier procedure, (Tessier et al. 1979), extracted with sodium acetate in acetic acid, may also be considered similar to diluted-acid fraction, and potentially available (Baeza et al. 2014). The bioavailable fractions, either readily or potentially available, for the anthropogenic and naturally occurring radionuclides in an ecosystem affected mainly by global fallout (see Fig. 2) are usually as follows:

- Readily available:
  ^{90}Sr $\gg$ ^{137}Cs, ^{226}Ra, $^{239+240}$Pu $>$ ^{238}U, ^{241}Am $>$ ^{40}K $>$ ^{210}Pb $>$ ^{232}Th
- Potentially available:
  ^{90}Sr $\gg$^{241}Am $>$ ^{210}Pb, $^{239+240}$Pu $>$ ^{226}Ra $>$ ^{137}Cs $>$ ^{238}U $>$ ^{40}K $>$ ^{232}Th

6 Modification of the Speciation of Radionuclides in Soil

The speciation of radionuclides in soil is not constant with time, due to weathering and the interaction with different soil components (Cheshire and Shand 1991; Krouglov et al. 1998; Baeza et al. 1999; Forsberg et al. 2001). It can also be modified by the addition of soil amendments and/or fertilizers, which can contain high content of naturally occurring radionuclides and other stable elements that can modify the soil equilibrium. In fact, fertilizers have been used as agricultural countermeasures to inhibit or at least decrease the transfer of anthropogenic radionuclides into produces. Their use is based on the saturation of the soil solution with the additional supply of nutrients chemically analogous to the released radionuclides from the fertilizers (Nisbet et al. 1993b); i.e., potassium for radiocesium and calcium for radiostrontium.

The application of potassium-based fertilizers decreases the ^{137}Cs:K ratio in the soil solution (Nisbet et al. 1993b; Zhu and Shaw 2000). At lower concentrations of potassium in soil solution ($<10^{-2}$–10^{-1} μM), the root uptake mechanism is unable to distinguish between Cs^+, Rb^+, and K^+ (Nisbet et al. 1993b; Shaw 1993; Zhu et al. 2000). However, at higher concentrations a critical threshold was observed, above which the root uptakes K^+ preferentially to Cs^+, 20 μM for wheat (Shaw et al. 1993). The application of these fertilizers reduced the soil-to-plant transfer of radiocesium about 40–60 % (Jacob et al. 2009; Rosén et al. 2011), and it was also observed during long periods of time, 10–34 year after fertilization (Kaunisto et al. 2002; Robison et al. 2009; Rosén et al. 2011). The addition of fertilizers that supply NH_4^+ can also modify the content of ^{137}Cs in the soil solution, increasing it by a factor of 3–4 (Nisbet et al. 1993b). The application of NH_4^+ and manure can also reduce the uptake of ^{137}Cs, due probably to the release of potassium and other ions from the manure when NH_4^+ is applied (Fuhrmann et al. 2003). The addition of phosphate stimulates root growth and may also increase the cesium uptake (Shaw 1993). The application of calcium to soils in order to reduce the radiostrontium transfer is usually by liming. Although the reduction is more limited than that of radiocesium, about 20 % of ^{90}Sr (Lembrechts 1993), because in some occasions the application of 1.6–15.6 ton Ca ha^{-1} was not able to modify significantly the calcium content in the soil solution (Vidal et al. 2001; Camps et al. 2004). The highest reductions were obtained in soils with low-calcium content (Shaw 1993).

Fertilizers, in particular those based on phosphate, can also have high contents of naturally occurring radionuclides, due to the initial content of phosphate rock and the industrial processes carried out in their production. Their worldwide range in NPK fertilizers are within (66–1,710) Bq kg^{-1} for ^{238}U, (1.5–451) Bq kg^{-1} for ^{226}Ra, (78–741) Bq kg^{-1} for ^{210}Pb, (28–307) Bq kg^{-1} for ^{232}Th, and (25–4,100) Bq kg^{-1} for ^{40}K (Mustonen 1985; Barišić et al. 1992; Righi et al. 2005; Saueia et al. 2005; Chandrajith et al. 2010; Chauhan et al. 2013). After the fertilizer application, interactions between it and the different soil components occur. There are many methods for analyzing the association of nutrients to fertilizers (CEE 1997), which can also be used to analyze the naturally occurring radionuclides in those fractions. The one used for extraction of water-soluble phosphorus in fertilizers consists in adding 5 g dw of fertilizer to 450 mL of distilled water at room temperature (20–25 °C), and stirred for 30 min (CEE 1977). The water-soluble fraction of a NPK fertilizer (NPK S (MgS) 6–10–18 S(3–36) with potassium from sulfates) showed that content of ^{238}U in that fraction was the highest, about 10 %, followed by ^{210}Po (8 %), and ^{226}Ra (1.6 %), being the ^{232}Th below detection limit (Baeza et al. 2011). However, this fraction can be leached by runoff water into surface and groundwater resources. Other chemical species, such as phosphates, nitrates, and sulfates, also showed increased levels in water bodies contaminated by use of fertilizers, leading to the eutrophication of water bodies (Zielinski et al. 1997; Badruzzaman et al. 2012). Although the application of phosphate-based fertilizers for long periods of time can increase the naturally occurring radionuclide content in soil, the uranium, radium, and thorium content in corn, leaves, grain, and wheat grown in lands using NPK fertilizer for years have been reported similar to those grown in non-fertilized (IAEA 2003).

Other by-products of the phosphate fertilizers industry (NORM), such as phosphogypsum, are also used as soil amendment. The content of radium, ^{210}Po, and ^{210}Pb in phosphogypsum is enriched due to the industrial processes usually carried out (Rutherford et al. 1994). They are usually accumulated in stacks, where are subject to weathering. The stack fluids might be considered as the fraction which has more similar to water-soluble fraction. The ^{226}Ra content in those fluids was lower than other naturally occurring radionuclides, such as uranium and ^{210}Pb (Burnett et al. 1996). The leaching of ^{226}Ra by rainwater has also been found to be a slow process (Haridasan et al. 2002). The ^{226}Ra was mainly associated with fine grains of phosphogypsum and very immobile (Rutherford et al. 1994; Hull and

Burnett 1996; Hull and Burnett 1996). The TF values of ^{226}Ra from soil amended with phosphogypsum to rice was of the same order of magnitude that the TF without phosphogypsum (Papastefanou et al. 2006).

7 Conclusion

The quantification of the soil-to-plant transfer of radionuclides, either anthropogenic or naturally occurring, by means of transfer factors or concentration ratios has some limitations. This is especially important to the ratios between what is in the plant and the soil consider the total content of radionuclides. Thus, their range of variation is about four orders of magnitude for the same plant groups. Soil dependence on the TF values has also been reported, which is correlated with the association of radionuclides to soil particles, and therefore their availability to be transferred.

The assessment of this association is usually carried out by speciation procedures, in which the soil is sequentially attacked by reagents with more replacement power. Water-soluble fraction and exchangeable fractions are usually the first fractions to be considered. The reagents used in later fractions depend on the characteristics of the study to be carried out. There a lot speciation schemes, some of them variations of the Tessier method (Tessier et al. 1979), which can make difficult the interpretation of the data. The results obtained by these procedures depend also on the radionuclide source, i.e., on the chemical form in which they were deposited. When they are attached to refractory particles, they are strongly attached to them, but this situation can vary with time. In the case of global fallout origin, the ^{90}Sr is the radionuclide which content is highest in the majority of the soil. The radiocesium is usually attached to clay minerals, which govern its bioavailability, lower than that of ^{90}Sr. Plutonium is frequently associated with organic matter in the soil. Naturally occurring radionuclides are mainly associated with fractions strongly fixed to the soil matrix, because they are found in minerals forming part of soil particles.

The use of fertilizers and soil amendments in agricultural practices can also modify the speciation of radionuclides in soil. This has been used in remediation actions by supplying stable elements chemically analogous to anthropogenic radionuclides, i.e., potassium to reduce the radiocesium transfer and calcium to reduce that of radiostrontium. Fertilizers, especially those produced from phosphate rock, can contain significant levels of naturally occurring radionuclides, which can also be transferred to plants. The radionuclides associated with the water-soluble fraction of the fertilizers can be leached out by runoff water and into water bodies. Phosphogypsum, a by-product of the phosphate fertilizer industry, can also be used as soil amendment, and usually presents a high level of radium. Its use did not increase the transfer of radium to plants.

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Radionuclide Uptake by Plants: Soil-to-Plant Transfer Factors, Kinetics of Absorption, and Internal Radionuclide Distribution of ^{137}Cs and ^{40}K in South American Species

Hugo Velasco, Roberto Meigikos dos Anjos and Jimena Juri Ayub

Abstract Soil-to-plant transfer factors (F_v) are commonly used as a key link to estimate the transference of radionuclides along the human food chain. The use of F_v assumes that the radionuclide concentration in plant is linearly related with the radionuclide concentration in soil. However, for different ecosystems and even considering similar soil type and plant species, a large variability in F_v values has been reported, showing that other variables in addition to radionuclide soil concentration have influence on the radionuclide uptake by plants. Another possible source of uncertainty in F_v could come from the heterogeneous distribution of the radionuclide in the plant. In this chapter, we analyze two situations: (a) the root uptake of Cs^+ and K^+ using electrophysiological techniques, for three grass species that grow in seminatural grassland of central Argentina and (b) the incorporation of ^{137}Cs and ^{40}K by tropical plants and their translocation to fruits. In both cases, we have considered components that are incorporated into the human food chain and, consequently, there is a need of adjusting their dosimetric contribution on the population.

Keywords Soil-to-plant transfer factor · ^{137}Cs · ^{40}K · Michaelis–Menten kinetics · Plant uptake

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Contents

1 Variability of Soil-to-Plant Transfer Factor

The consumption of fruits and vegetables containing radionuclides represents the main way of radionuclide intake by humans and concomitant internal exposure (Shaw and Bell 2001). Primarily, the plants incorporate radionuclides through root absorption; the radionuclide transference from soil to vegetation is usually modeled using the soil-to-plant transfer factor (F_v). For a particular radionuclide, F_v is defined as (IAEA 2010):

$$F_v = \frac{\text{Activity concentration in plant (Bq kg}^{-1}\text{ dry mass)}}{\text{Activity concentration in soil (Bq kg}^{-1}\text{ dry mass in upper 10 or 20 cm)}} \tag{1}$$

F_v values have been collected in databases developed by the US Nuclear Regulatory Commission (Ng et al. 1979) and the International Union of Radioecology (Frissel and van Bergeijk 1989; Frissel et al. 2002). These data were gathered mainly for temperate regions belong to Northern Hemisphere as a consequence of Chernobyl incident. The International Atomic Energy Agency recently published the largest database available today of radionuclide transfer coefficients in terrestrial and freshwater environments, including information of tropical and subtropical environments and regions of the Southern Hemisphere (IAEA 2010). The large number of observations that have been accumulated demonstrates that, for most radionuclide, particularly for those of long-lived, soil-to-plant transfer factors show variations, which may exceed three orders of magnitude (Frissel 2002; Velasco et al. 2008a). In fact, Velasco et al. (2008b) analyze more than 2,700 F_v values from tropical and subtropical environment with the purpose of exploring the influence of crop types and soil properties on radionuclide uptake by plants. They conclude that F_v values for ^{137}Cs present differences of five orders of magnitude. Even when the same group of plants and soil type are evaluated, the F_v variability is wide. In temperate woody trees, for instance, F_v values for radiocesium range from 8.6×10^{-4} to 8.0×10^{-2} (Carini 2009; IAEA 2010). In contrast, they range from 5.0×10^{-2} to 8.7 in tropical and subtropical environments (IAEA 2010; Velasco et al. 2008b). While this variability has been recognized by many authors, different hypotheses have been proposed to understand and reduce the uncertainty

(Frissel and van Bergeijk 1989; Ehlken and Kirchner 1996, 2002; Ciuffo et al. 2002; Velasco et al. 2004; Carini et al. 2005). This wide variability suggests that other variables, besides soil concentration, would influence the amount of radionuclide to be uptaken by the plant. The large number of parameters involved and the interdependence between them, make it difficult to assess the effect of each single factor on the entire transfer process.

Considering these constraints in the use of F_v, in this study, we incorporate two situations that can give some answers to reduce the F_v uncertainty. The first is to explore the cellular mechanisms that influence the uptake by plants of monovalent ions, such as Cs^+ and its chemical analogue K^+. Three grass species (*Distichlis spicata*, *Eragrostis curvula,* and *Cynodon* sp) growing in seminatural grassland of central Argentina were selected to investigate their capability to incorporate these cations using electrophysiological techniques (Juri Ayub et al. 2008). Kinetic experiments indicated the presence of high-affinity transport systems for the uptake of potassium and cesium in the roots of the analyzed species. Both potassium and cesium uptake data were fitted to Michaelis–Menten model, and the parameters obtained in both cases are comparatively analyzed. Also, for one species, *Cynodon* sp, the competitive effect of K^+ addition on Cs^+ uptake by roots was evaluated. Both ions compete for the union sites of the same carriers, but do not behave as strict analogues. That could explain the differences observed in F_v for K^+ and Cs^+, considered a priori with similar environmental behavior from a radioecological viewpoint.

In the second situation, we evaluate the soil uptake of ^{137}Cs and ^{40}K by tropical plants and their consequent translocation to fruits. The changes in ^{40}K and ^{137}Cs activity concentrations during the fruit growth of lemon tree were followed from gestation to maturity. A mathematical model was calibrated from the experimental data allowing simulating the radionuclide incorporation by fruits. Although the fruit incorporates much more potassium than cesium, both radionuclides present similar absorption patterns during the entire growth period. Considering the manner in which plants absorb elements present in the soil, and the complex internal distribution of these elements in different parts of plants, it would be possible to reduce the F_v variability and diminish the uncertainty when food chain models are used to approach the radionuclide content in each compartment.

2 Cs^+ and K^+ Kinetics of Absorption

Three grass species grown in seminatural grassland of central Argentina: *Eragrostis curvula*, *Cynodon* sp, and *Distichlis spicata* were selected to explore the capability to incorporate the monovalent cations Cs^+ and K^+. These plants grow in soils in which ^{137}Cs fallout inventory range from 328 to 730 Bq m^{-2}, and ^{40}K specific activity range from 740 to 770 Bq kg^{-1}. Individuals of *Cynodon* sp and *D. spicata* were extracted from the field and cultivated in hydroponic culture.

Table 1 Michaelis–Menten kinetics parameters for potassium and cesium uptake by root cells

Parameters	*D. spicata*		*Cynodon* sp		*E. curvula*	
	K^+	Cs^+	K^+	Cs^+	K^+	Cs^+
D_{MAX} (mV)	18.4 ± 0.9	13.7 ± 1.5	21 ± 3	12 ± 2	56.6 ± 4.4	37.0 ± 4.1
K_M (μM)	97.4 ± 16.2	163.3 ± 51.9	73.3 ± 34.1	120.2 ± 52.7	142 ± 48	607 ± 268
R^2	0.98	0.95	0.81	0.91	0.98	0.99

Commercial seeds of *E. curvula* were germinated in distilled water and later transferred to hydroponic culture (Juri Ayub et al. 2008). Previously to electrophysiological experiments, all plants were submitted to K^+ starvation for three days. Membrane potentials (E_m) were determined by electrophysiology techniques (Heredia et al. 2002), and variations of this parameter were recorded at different external potassium or cesium concentrations. Changes of the membrane potential (E_m) can be considered an estimate of ion uptake, and these data could be fitted to the Michaelis–Menten equation:

$$V = \frac{V_{\mathrm{MAX}}\, S}{K_M + S} \tag{2}$$

where S (μM) is the substrate concentration in assay medium; V (estimated by ΔE_m, in mV) is the uptake by cell root, V_{MAX} (estimated by D_{MAX}, maximum depolarization, in mV) is the maximal rate of uptake by cell root, and K_M (μM) is the Michaelis–Menten constant. High-affinity transport systems (System 1) were detected for the uptake of potassium and cesium in the roots of the three analyzed species. Both potassium and cesium uptake data were fitted to Michaelis–Menten model, showing R^2 values higher than 0.8 (Table 1). In all plants, the affinity constant, K_M, was smaller for K^+ than for Cs^+, indicating the higher affinity of the carriers for K^+ than for Cs^+. Both ions compete for the union sites of the same carriers, but do not behave as strict analogues, as indicated also by the values of $D_{\max}$ that were always lower for Cs^+ than for K^+.

Direct effect of increasing K^+ concentrations on Cs^+ uptake was evaluated in *Cynodon* sp (Fig. 1). In culture medium without K^+, the addition of a saturating concentration of Cs^+ (0.5 mM) induced a membrane depolarization of 14 mV (Fig. 1, left side). This depolarization value was similar to maximum depolarization obtained in Cs^+ uptake kinetic experiments (Table 1). However, in the presence of 0.5 and 1 mM of K^+ in the assay medium, the addition of Cs^+ (0.5 mM), after membrane potential stabilization, caused a depolarization 3- and 7-fold lower, respectively, than in the absence of K^+ (Fig. 1, middle). The addition of 0.5 mM Cs^+ at 5 mM K^+ did not induce a clear depolarization. An increase in external K^+ concentration causes then a decrease in the absorption of Cs^+. This effect is due to the competition of both ions for union sites of high-affinity potassium carriers, as it has been shown for these transporters (Heredia et al. 2002).

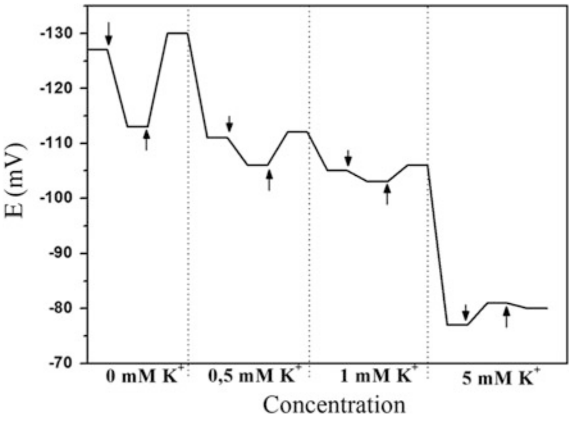

Fig. 1 Membrane potential depolarization induced by addition of 0.5 mM Cs$^+$ (*downward arrow*), in culture medium containing increasing K$^+$ concentration. *Upward arrows* show onset of Cs$^+$ wash (Juri Ayub et al. 2008)

The relative permeability of the cellular membrane to these two ions was analyzed for *D. spicata* and *Cynodon* sp. The relative permeability was estimated to be 0.74 and 0.71, respectively. These findings indicate that the membranes of the root cells of the species analyzed are highly permeable to Cs$^+$, being around 70 % of K$^+$ permeability.

3 Radionuclides Internal Distribution in Plants

As was previously emphasized, when the transfer factors are assessed, the procedure presumes that the concentration in the plant compartment and in the soil remains constant over time. That implies that if food chain model is applied, the steady state in radionuclide concentration in each compartment is assumed (Ng et al. 1979). This condition is acceptable for the radionuclide soil concentration, but it could be a severe limitation for inaccurate analysis about the radionuclide content in part of the plants. A typical deviation to this behavior occurs particularly when the incorporation of radionuclides by fruits is evaluated. They can be consumed at various stages of their growth and the specify activity usually changes strongly during this period.

In this section, we analyze the changes in ^{40}K and ^{137}Cs activity concentrations during the growth of tropical lemon fruits (*Citrus limon*) from gestation until maturity. The experiments were performed at the Laboratório de Radioecologia e Alterações Ambientais (LARA) of the Instituto de Fisica of Universidade Federal Fluminense using lemon trees grown in Goiânia region, in central Brazil, where in 1997, there was a radiological accident involving a source of ^{137}Cs (IAEA 1988; Anjos et al. 2002, 2007, 2009a, b; Carvalho et al. 2006; Mosquera et al. 2006). The soil profile was analyzed from the surface to 50 cm deep, in 5-cm-thick layers. Soil samples were dried, submitted to a homogenization process, and sieved in order to separate the soil particles from the stones, grass, roots, and other organic materials.

The fruit samples were washed with distilled water, dried in stove at 105 °C, and finally were ground to powder. Afterward, all samples were packed into cylindrical plastic containers, dry-weighed, and sealed. The amounts of ^{137}Cs and ^{40}K in the soil samples were determined by standard gamma spectrometry. The presence of potassium in fruit samples was quantified by neutron activation analysis (NAA) performed at the IEA-R1 research reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP). Samples were bombarded with neutrons, resulting in the production of radioactive isotopes of the elements of interest. Gamma rays emitted by the radioactive isotopes were then analyzed by gamma-ray spectrometry.

The activity concentration of ^{137}Cs and ^{40}K in lemon fruit was evaluated at different times (Table 2). The fruit dry mass for each time and the radionuclide activity concentration in the 20 cm of top soil are also indicated.

Data obtained were used to calibrate a mathematical model for describing the growth dynamics of fruits and the temporal evolution of the soil-to-fruit transfer factor (Velasco et al. 2012; Cid et al. 2013). The model assumes that fruit dry mass grows according to a logistic model taking into account two main assumptions:

- The growth curve of the fruit dry matter follows the differential equation:

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = \alpha M(t)[M_m - M(t)] \tag{3}$$

where M is the fruit dry mass (g), t the time (d), α the maximum growth rate (d^{-1}), and M_m *the maximum value of M(t)*. The solution to Eq. (3) is

$$M(t) = \frac{M\,M_m}{(M_m - M_0)\exp(-\alpha t) + M_0} \tag{4}$$

where $M_0 = M(0)$.

- The radionuclide activity concentration in fruits decreases exponentially following the differential equation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\beta(C - C_{\min}) \tag{5}$$

where C is the radionuclide activity concentration in fruit (Bq kg^{-1}), β is the exponential decreasing parameter (d^{-1}), and $C_{\min}$ is the minimum radionuclide activity concentration value (Bq kg^{-1}). Its solution is

Table 2 Radionuclide activity concentration in fruit and soil (20 cm) during the fruit development

Time (d)		20(7)	60(7)			90(7)		120(7)	140(7)		160(7)
^{137}Cs	Fruit	209(25)	114(15)			93(13)		83(13)	76(12)		83(13)
(Bq kg^{-1} dw)	Soil	3659(292)									
Time (d)		16(7)	31(7)	49(7)	55(7)	71(7)	87(7)	113(7)	129(7)	158(7)	165(7)
^{40}K	Fruit	805(105)	637(48)	482(57)	422(38)	440(25)	422(51)	407(44)	365(35)	437(48)	431(47)
(Bq kg^{-1} dw)	Soil	792(32)									
Fruit dry weight (g)		0.117(0.05)	0.523(0.16)	0.847(0.16)	3.08(0.5)	3.92(0.83)	5.17(0.65)	7.39(1.0)	10.28(1.3)	18.9(2.0)	17.22(2.0)

The values given in parentheses indicate the error associated with each measure

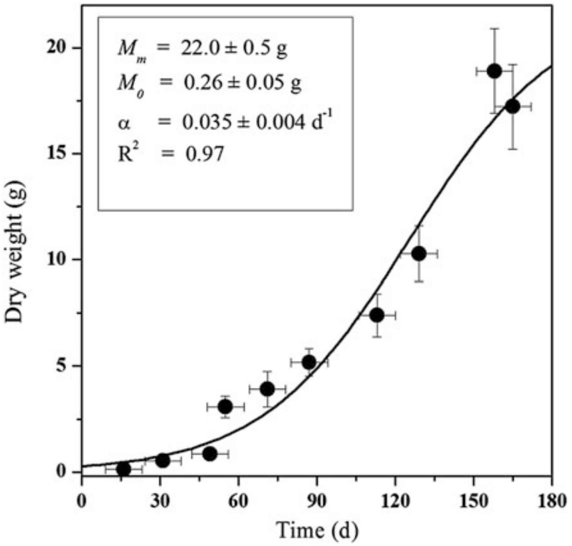

Fig. 2 Fruit dry weight as a function of time. Measurements and theoretical approach (Velasco et al. 2012; Cid et al. 2013)

$$C(t) = C_r \exp(-\beta t) + C_{\min} \tag{6}$$

where $C_r = C(0) - C_{\min}$.

From the multiplication of Eq. 13.5 and 13.6, the radionuclide activity (Bq) in the entire fruit as a function of time can be obtained as

$$A(t) = M(t) \times C(t) \tag{7}$$

For this case, the soil-to-fruit transfer factor (F_v) is (Eq. 1)

$$F_v = \frac{\text{Concentration of radionuclide in fruit (Bq kg}^{-1}\text{ dry mass)}}{\text{Concentration of radionuclide in soil (Bq kg}^{-1}\text{ soil dry mass in upper 20 cm)}} \tag{8}$$

Assuming that the radionuclide activity concentration in soil does not change during the fruit growth period, then the soil-to-fruit transfer factor is

$$\begin{aligned} F_v(t) = \frac{C_F(t)}{C_S} &= \frac{C_{Fr}}{C_S} \exp(-\beta t) + \frac{C_{Fvmin}}{C_S} \\ &= F_{vr} \exp(-\beta t) + F_{vmin} \end{aligned} \tag{9}$$

where $F_{v\min}$ is the minimum value of F_v and the sum $F_{vr} + F_{v\min}$ is the maximum value of the soil-to-fruit transfer factor.

The theoretical approach for describing the growth of the fruit dry mass (Eq. 3) has been represented in Fig. 2. The parameter values obtained from the model calibration are showed in the same figure. Fruit development shows a sigmoidal growth with a maximum growth rate around $t = 100$ d. After the time $t = 160$ d,

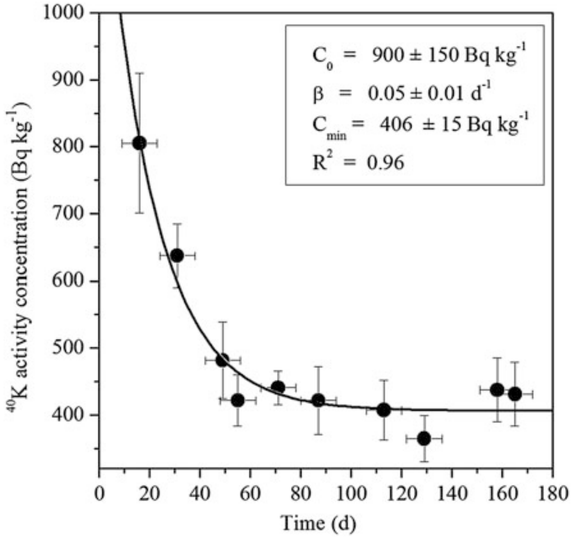

Fig. 3 ^{40}K activity concentration in fruit as a function of time. Measurements and theoretical approach (Velasco et al. 2012; Cid et al. 2013)

the growth rate decreases, reaching the fruit the final stage, with a dry mass of 18–19 g.

Figures 3 and 4 show ^{40}K and ^{137}Cs activity concentration in fruit, respectively, for the entire development period, and the curves represent the theoretical approach. The values of β is the same for both radionuclides suggesting a similar behavior in which the fruit incorporates both cations (Delvaux et al. 2000; White and Broadley 2000; Zhu and Smolders 2000). Robison et al. (2009), studying the changes in ^{40}K and ^{137}Cs concentrations in the development of coconut trees fronds, find a similar decrease in radionuclides concentrations, for plant grown in low potassium content in soil. These plants show a retrieval of K^+ and Cs^+ from the fronds to the plant when leaves reach maturity and senescence. Although fruits and leaves are not physiologically identical, our results show that in the development of lemon fruits, some potassium and cesium are recovered by the plant when they reach maturity, similar to what occurs in coconut leaves.

The rate of ^{40}K and ^{137}Cs incorporation by lemon fruits is represented in Fig. 5 (Eq. 7), the derivative function of $A(t)$. This figure shows the greater preference for the fruits to absorb ^{40}K in relation to ^{137}Cs throughout the growth period. Although the same transport mechanisms are implicated in the transfer of ions to fruit, differences in the uptake rates has been reported for several plant species between both potassium and cesium, showing the plant capability for discriminating between potassium and cesium, preferably by the first ion (Shaw and Bell 1989; Juri Ayub et al. 2008).

Finally, in Fig. 6, we represent F_v as a function of time. The theoretical curves have been obtained from Eq. 9. The characteristic factor of the exponential decreasing function ($\beta = 0.5$) is the same for both radionuclides. At the beginning

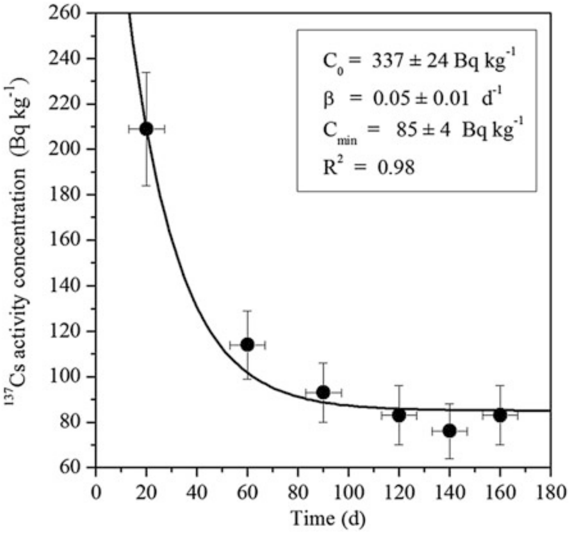

Fig. 4 ^{137}Cs activity concentration in fruit as a function of time. Measurements and theoretical approach (Velasco et al. 2012; Cid et al. 2013)

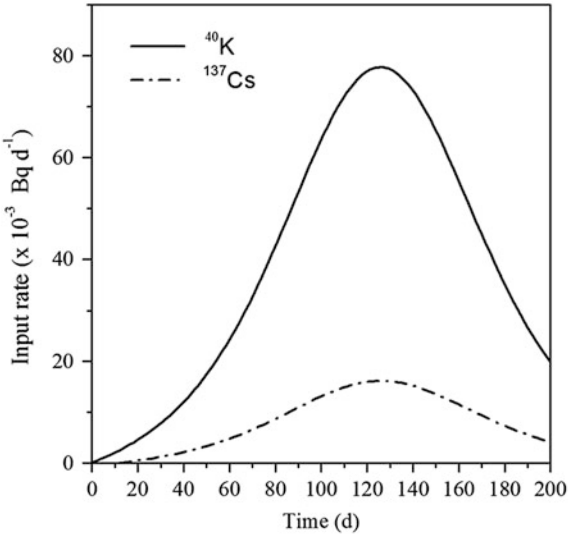

Fig. 5 ^{40}K and ^{137}Cs uptake rate by fruit as function of time. These theoretical approaches represent the temporal derivative of the function AT(t) given by Eq. (7) (Velasco et al. 2012; Cid et al. 2013)

of fruit development period, F_v is about 17 times greater for ^{40}K than for ^{137}Cs. In the maturing period, this difference seems to increase, being the soil-to-fruit transfer factor for ^{40}K about 25 times higher than for ^{137}Cs.

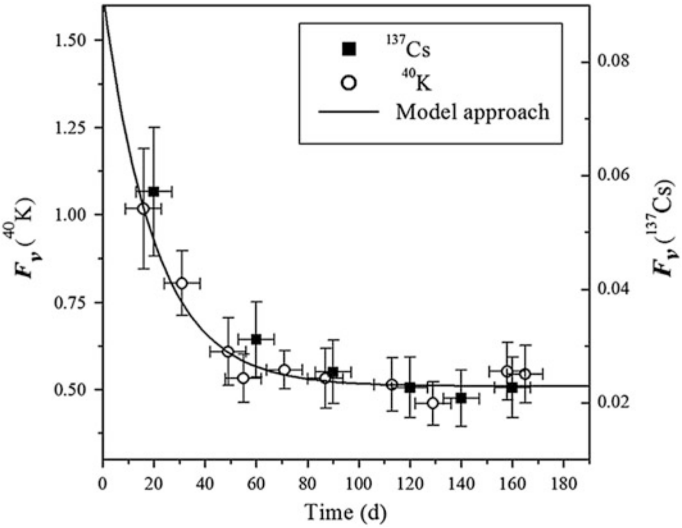

Fig. 6 Temporal dependence of ^{137}Cs and ^{40}K soil-to-fruit transfer factor for tropical lemon trees (Velasco et al. 2012)

4 Conclusions

Soil-to-plant transfer factors are commonly used as a key link to estimate the transference of radionuclides along the human food chain. The use of F_v in the calculations of this transfer involves the assumption that the radionuclide concentrations in plant and in the rooting zone of the soil are linearly related. However, this condition usually involves an oversimplification. Physical, chemical, and biological mechanisms occur both in the absorption process of radionuclides by root and in the process of redistribution of radionuclides in different parts of the plant. That makes this linear relationship is usually not satisfied or that the dispersion in the F_v measured values is extremely wide.

In this study, we explore two situations that can help us to partially explain this uncertainty and thus reduce it. In the first, grass species grown in seminatural grassland of central Argentina were selected to follow their capability to incorporate the monovalent cations Cs^+ and K^+. The results obtained show that the permeability of the membrane of the root cells to Cs^+ is almost 70 % of K^+ permeability, indicating that potentially cesium can be incorporated in plant when is available in soil.

On the other hand, plants have a high-affinity system to uptake potassium and cesium. The transport of both ions are carried out by the same potassium carriers, but showing a lower affinity for Cs^+ and also a lower maximum uptake rate. Electrophysiological experiment allows detecting interspecific differences in V_{MAX} and K_M for K^+ and Cs^+ uptake, as it has been described for Cs^+ uptake kinetics in another grass species.

In addition, we have shown that addition of K^+ to assay culture decreases strongly Cs^+ uptake in *Cynodon* sp. The external concentration of K^+ has then a direct influence on Cs^+ incorporation by plants. Kinetic studies of Cs^+/K^+ interaction can help us to understand the wide variability detected in transfer factors and could also provide a screening procedure to select plants with different cesium affinities, for example with low cesium uptake capacity.

In the second situation, we explore the ^{137}Cs and ^{40}K soil-to-fruit transfer factor for tropical lemon trees. We conclude that F_v for ^{40}K, at the initial stage of fruit development, is more than twice that in the fruit maturation stage, while F_v for ^{137}Cs is three times higher. In spite of the chemical analogies between potassium and cesium, F_v is at least one order of the magnitude higher for ^{40}K during the entire fruit development period. However, the temporal pattern for radionuclides incorporation by fruits was very similar for both radionuclides. The logistic model was applied to describe the dry mass growth for fruits. The corresponding parameters were obtained when compared with experimental data. The fruit growth is a dynamic process and determines the degree of contamination by radionuclides. This is of fundamental importance because it involves the edible part of the plant, and any radionuclide content is transferred to the consumer.

A theoretical approach was introduced describing the evolution of ^{40}K and ^{137}Cs activity concentrations in fruits as a function of time. The agreement with the experimental data is satisfactory. Then, the radionuclide input rate was calculated for both radionuclides. Finally, the transfer factor was determined for the entire growth period, demonstrating its temporal variability.

In the explored cases, the agreement between the experimental data and the theoretical approach is very good. The results could be a significant advance in the modeling of nutrients accumulation by fruits and the explanation of the variability of the radionuclide soil-to-fruit transference.

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Impact of Plant Growth in Waste-Contaminated Areas

G. H. Ben-Bolie, P. Ele Abiama and P. Owono Ateba

Abstract This chapter presents the influence of radionuclides on the plant growth with particular emphasis on phytoremediation technology for radioactive decontamination. After radiological catastrophe, radionuclide fallout can contaminate soil, leading potentially to higher radiation exposure of human population. Most of the conventional remedial technologies are expensive and inhibit the soil fertility; this subsequently causes negative impacts on the ecosystem. It is shown in this review that phytoremediation is a cost-effective, environmentally friendly, aesthetically pleasing approach most suitable for radioactive decontamination waste area. This chapter reports how physical, chemical processes, and biological accumulation influence the destiny of radionuclides in plants. A case study showed that accumulation properties of common reed could be useful in phytoremediation of mine waters or for bioindication of radionuclides in such waters. High-activity concentrations of radionuclides in the U-mill tailings did not negatively impact on plants growth. This means that common reed belongs to the metal-resistant plants with a metal-tolerance mechanism against toxic elements.

Keyword Radionuclides · Phytoremediation · Contaminated soil · Radioactive waste · Plants · Vegetal hormones · Vegetal enzymes

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Contents

1 Introduction

Contamination of soil with radionuclides is a worldwide problem, which has developed over the last twenty years in line with the development of nuclear technology itself. Physical approaches to eliminate or cleanup polluted sites have often proved to be prohibitively expensive. Agriculture-based counter measures, such as application of phytoremediator plants, have been proven to be effective in reducing the transfer of radionuclides from soil to plants in agricultural production systems with low levels of contamination. However, further investigation is still needed to optimize these counter measures with bioremediation in order to have better results. The natural or artificial release of radionuclides can potentially lead to radiation exposure of surrounding biota and human population. Radioactivity waste that is released and dispersed into the atmosphere enters the terrestrial environment due to dry and wet deposition into soil and vegetation, causing exposure of either human or biota. It is then important to know whether radionuclides interfere in plant growth. So, the study of radionuclides in agricultural areas is of general concern. Plants uptake of radionuclides will depend on interactions between radionuclides and soil and will also depend on the metabolic and physiological characteristics of the species. Elements absorbed by plants through the root system (indirect contamination) or through the aerial organs (direct contamination) may be redistributed within plants. There are considerable differences in the uptake and translocation of long-lived radionuclides among different plant species. Radionuclides are transported to specific tissues based on the function of the element in plant metabolism and are reflected in its higher concentration in a particular part compared with other parts. Radionuclides can also be

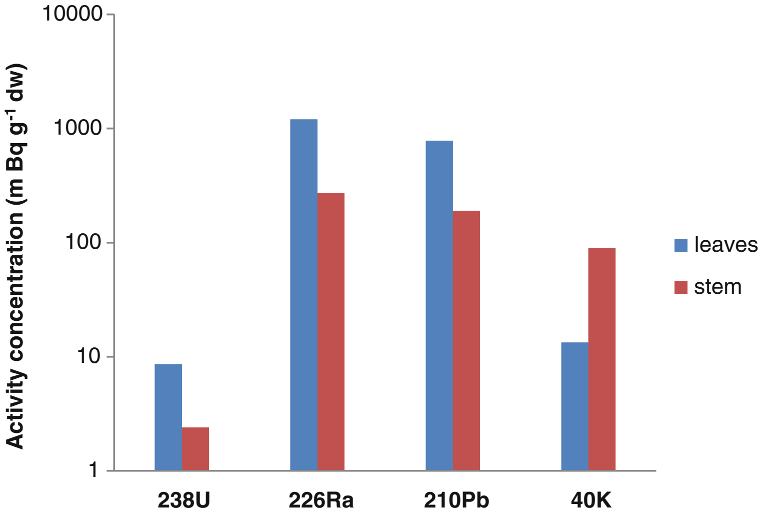

Fig. 1 Radionuclide content in leaves and stems of plants (common reed) form the study site

picked up along with nutrients and may have similar chemical behavior as the essential nutrient. In order to study the translocation and preferred site of accumulation of a radionuclide, the total content of a radionuclide in the whole plant was normalized for dry weight fraction of each part (IAEA 2006; Pöschl et al. 2007; Ben-Bolie 2008; Ele et al. 2010; Salahel Din et al. 2010; Ele et al. 2012) (Fig. 1).

1.1 Type of Phytoremediator Plants for Radionuclide Decontamination

Phytoremediation is an emerging technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soils and water. This technology has been receiving attention lately as an innovative, cost-effective alternative to the more established treatment methods used at hazardous waste sites. It has been suggested as an efficient method for decontaminating soil from radionuclides, whereas sorbents have been widely used for water treatment (Kremlyakova and Komarevsky 1997; Zhu and Shaw 2000). Phytoremediation is a most desirable technology that uses plants to remove environmental pollutants. Many living organisms can accumulate toxin concentrations that are much higher than they are in their environments (Ben Chekroun et al. 2013). Phytoremediation has many benefits over other soil remediation techniques. Since phytoremediation is the situ, it is easier to use and is cheaper than most other remediation techniques. Results from greenhouse studies need to be tested in outdoor environments to determine

Table 1 Radionuclide concentrations in the deposit tailings (expanded uncertainties, $k = 2$)

(Bq g^{-1} dry weight)	^{238}U	^{226}Ra	^{210}Pb	^{40}K
Bor št	1.38 ± 0.28	14 ± 2.0	7.1 ± 4.6	0.78 ± 0.14
Jazbec	0.07 ± 0.02	0.056 ± 0.008	<0.15	0.42 ± 0.08

Table 2 Activity concentrations in leaves and stems of plants (average of 20 plants) grown at the study site (expanded uncertainties, $k = 2$)

(m Bq g^{-1} dry weight)	^{238}U	^{226}Ra	^{210}Pb	^{40}K
Leaves	8.6 ± 0.8	1200 ± 100	780 ± 10	13.3 ± 0.5
Stems	2.4 ± 0.2	270 ± 20	190 ± 10	90 ± 4

Table 3 Activity concentrations in leaves and stems of control plants (average of 20 plants) grown in the marsh in the vicinity of Ljubljana, the capital (expanded uncertainties, $k = 2$)

(m Bq g^{-1} dry weight)	^{238}U	^{226}Ra	^{210}Pb	^{40}K
Leaves	2.7 ± 0.11	<0.04	<10	630 ± 11
Stems	0.3 ± 0.1	1.0 ± 0.2	<10	780 ± 14

their effectiveness. Outdoor experiments should include various soil amendments to see which amendments favor increased radionuclide uptake in the outdoors. However, the potential for mycorrhizal plants to be an effective remediation strategy for radionuclides appears great and will likely be enormously beneficial in cleaning environments contaminated by recent nuclear accidents. The plants used in the phytoremediation technique must have a considerable capacity of radionuclides absorption. They are many techniques to moderate the storage of contaminants, namely: phytosequestration, phytodegradation, phytovolatilization, phytostabilization, and phytoextraction (Victor et al. 2004) (Tables 1, 2, 3).

1.1.1 Phytosequestration

The following three phytosequestration mechanisms reduce the mobility of contaminants and prevent their migration to the soil, water and air (Prasad 2011):

1. Phytochemical complexation in the root zone: Phytochemicals can be secreted into the rhizosphere, leading to the precipitation or immobilization of target contaminants in the root zone. This phytosequestration mechanism can reduce the fraction of the contaminant that is bioavailable.
2. Transport protein inhibition on the root membrane: Transport proteins associated with the exterior root membrane can irreversibly bind and stabilize contaminants on root surfaces, preventing contaminants from entering the plant.

3. Vacuolar storage in the root cells: Transport proteins are also present to facilitate the transfer of contaminants between cells. However, plant cells contain a compartment (vacuole) that partially acts, as a storage and waste receptacle for plants. Contaminants can be sequestered into the vacuoles of root cells, preventing further translocation to the xylem.

1.1.2 Phytodegradation

The breakdown of contaminants by plants occurs either internally through metabolic processes within a plant or externally through the release of compounds (such as enzymes) produced by a plant. Pollutants can be degraded, incorporated into the plant tissues, and used as nutrients. Even though chemical forms can be degraded, radionuclides cannot be altered except through their fixed radioactive decay process cannot be accelerated or decelerated (Victor and Denise 2004).

1.1.3 Phytovolatilization

The uptake and transpiration of a contaminant by a plant is followed by the release of the contaminant or a modified form of the contaminant to the atmosphere from the plant. Phytovolatilization occurs as growing trees, and other plants take up water along with the contaminants. Some of these contaminants can pass through the plants to the leaves and volatilize into the atmosphere at comparatively low concentrations (Prasad 2011):

1.1.4 Phytostabilization

Photostabilization is the use of certain plant species to immobilize contaminants in the soil and groundwater through absorption and accumulation in plant tissues, adsorption into roots, or precipitation within the root zone. This process reduces the mobility of the contaminant by retarding migration to the groundwater or air and by reducing bioavailability for penetration into the food chain. This technique can be used to reestablish a vegetative cover at sites where natural vegetation is lacking due to high radioactivity concentrations in surface soils or physical disturbances to surficial materials. Radioactivity-tolerant species can be used to restore vegetation to such sites, thereby decreasing the potential migration of contamination through wind erosion, transport of exposed surface soils, and leaching of soil contamination to groundwater (Prasad 2011):

1.1.5 Phytoextraction

Phytoextraction is the uptake and translocation of radioactive contaminants, by plant roots into the above-ground portions of the plants. Some plants referred to as hyperaccumulators absorb unusually large amounts of radionuclides. One or a combination of these plants is selected and planted at a site depending on the type of radionuclides present and other conditions of the site. After the plants have been grown to a predetermined size, age or growth stage, they are harvested and tested for radioactive content. The radioactive content of the plant, value of the material, half-life, and regulations then determine the appropriate means of disposal of radioactive plant matter which can be either through solid waste recycling or hazardous waste disposal. In some cases, plants may be dried, composted, or incinerated to a reduced volume (Prasad 2011).

2 Effective Phytoremediator Plants for Radioactive Decontamination

2.1 Mycorrhizal Associations

Mycorrhizae are the symbiotic relationship between a soil-borne fungus and the roots of a plant. Mycorrhizal fungi depend on host plants for carbon and in return they enable host plants to be more efficient in acquiring nutrients and water from the soil. There are two types of mycorrhizal fungi, namely ectomycorrhizae and endomycorrhizae. Ectomycorrhizae form sheaths around plant roots. Endomycorrhizae enter cortex cells in the plant roots (Rost et al. 1998; Entry et al. 1999). Although certain plant species that are normally symbiotic with mycorrhizal fungi can exist without the fungal association, the fungus greatly enhances the plant's growth. Hosting mycorrhizae is much more energy effective to the plant than producing plant roots (Marshall and Perry 1987). A study done by Harley (1989) found that most roots need about 100 times the amount of carbon than do the hyphae of its associated ectomycorrhizae in order to span across the same amount of soil. Therefore, it is easier for hyphae to acquire elements that have a low mobility than it is for plant roots cesium-137 and strontium-90 both has low mobilities. Most arbuscular mycorrhizae do not have specific host plants. Hence, if the area that is going to be remediated already has well established angiosperms, it may not be necessary to add fungal spores to that area because they probably already exist in the soil. If plants are not growing on the site, it may however be beneficial to add mycorrhizal spores to the soil in order to increase colonization (Kirk and Staunton 1989; Entry et al. 1999). Inoculating potted plants in the nursery such as tree seedlings with specific mycorrhizae may also be a good idea if a specific type of mycorrhizal fungi is desired, for some types have been shown to work better than others. Inhibition of mycorrhizal growth can occur due to high phosphate levels in the soil (Entry et al. 1994; Killham 1995).

2.2 Sunflowers

These plants were effective in phytoremediation for radioactive decontamination in groundwater and waste water in several areas of the world following the example of USA and Ukraine at Chernobyl.

2.3 Other Types of Phytoremediator Plants

These include trees, Pfitzer junipers, Redroot Pigweed, Indian mustard, Semiarid prairie, Native cottonwoods, Hybrid poplar, which are also effective in remediation of soils, groundwater, and water when they have undergone radioactive contamination.

3 Destiny of Radionuclides in Plants

When radionuclides are produced and deposited randomly in the atmosphere by radioactivity whether by wet or dry deposition processes, some fraction of the produced elements are intercepted by vegetation, while the rest fall back to the ground. Some of the radionuclides intercepted by the vegetation, bounce off, roll-off are washed off to the ground, while the rest is retained on the surface of the vegetation. The fraction of radionuclide initially retained (i.e., not immediately blown or washed off) by vegetation is referred to as the interception fraction f. Chamberlain (1970) provided a relationship between the interception fraction f and the standing biomass B.

$$f = 1 - e^{-\mu B} \tag{1}$$

where B is above-ground biomass (dry weight) of vegetation per unit area (kg m^{-2}) and μ the absorption coefficient (m^2 kg^{-1}). To account for the variation in different values of B, some authors analyze results in terms of μ, and others in terms of a mass interception factor f/B. If f is less than about 0.3, there is practically little difference between f/B and μ (e.g., $f = 0.3$, $f/B = 0.3/B$, $e^{-\mu B} = 0.7$, $\mu = 0.36/B$). According to Chamberlain, when f approaches unity, (as that may be the case when B is large), it is more appropriate to use μ. For this, it is very important to follow their evolution in plants because they emit radiation. However, it should be noted that in many cases, it is not easy to estimate the direct radionuclide concentrations within plants.

3.1 Radionuclides in Plants

Public exposure to radiation from natural radioactive decay series is due mainly to the fact that the latter dissolves in water and migrates to surface of water reservoirs, thereby contaminating plants through soil to plant transfer which is then ingested into the human body (Al-Kharouf et al. 2008; Ele et al. 2012). Exposure to radionuclides in plants varies according to soil type, chemical characteristics, and radionuclide uptake by specific plants. Radionuclides in soils are frequently transferred to different plant tissues by direct transfer via the root system or by fallout of radionuclides and resuspension of contaminated soil followed by deposition on plant leaves. Consequently, relationships between substrate (soil) and plant concentrations for both nutrients and contaminants were widely studied (Shanthi et al. 2010; Ben-Bolie et al. 2013).

(a) **Physical and chemical processes**

Once released into air or water, radionuclides are influenced by physicochemical processes that lead to their advection and dispersion in the environment. The physical and chemical forms of the radionuclide and the turbulence of the receiving medium both play an important role in relation to these initial transport mechanisms. Other processes continually cause the transfer of contaminants from the air or the water column to the ground or sediment surface.

In the terrestrial environment, the interception of radionuclides by vegetation occurs by wet and dry deposition; radionuclides may also be deposited to the ground directly. Biomass per unit area clearly affects the interception fraction for all deposition categories, but other factors, including ionic form, precipitation intensity, vegetation maturity, and leaf area index are especially important when considering wet deposition. Radionuclide concentrations on vegetation may be reduced by a number of physical processes, including wash-off by rain or irrigation, surface abrasion and leaf bending from wind action, resuspension, tissue senescence, leaf fall, herbivore grazing, growth, and evaporation (Pröhl 2009; Ben-Bolie et al. 2013). Various empirical formulae have therefore been derived to model the retention of radionuclides on vegetation (IAEA 1994, 2009). Physical, chemical, and biological processes occurring in soil and sediment lead to the further redistribution of radionuclides within these compartments. In soils, radionuclides can migrate to deeper soil depths by leaching. Rates of leaching are greatest under conditions of high rainfall and for soils containing a relatively large proportion of sand particles (Copplestone et al. 2001). Rainfall intensity is also a factor that influences leaching rates. Depending on the site-specific characteristics of the watershed, in poorly buffered water surfaces, acidic snowmelt can also solubilize radionuclides, resulting in increased water concentrations at some periods of the year. The migration of a chemical element in a fluid is governed by the following equation (Ema'a et al. 2012; Ema'a 2014):

$$\frac{\partial C}{\partial t}+U\frac{\partial C}{\partial x}+V\frac{\partial C}{\partial y}+W\frac{\partial C}{\partial z}=\frac{\partial}{\partial x}\left(k_x\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(k_y\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(k_z\frac{\delta C}{\delta z}\right)+S \quad (2)$$

which is a three dimension equation. Where $\frac{\partial C}{\partial t}$ (Bq kg^{-1} s^{-1}) is the variation of concentration of the fluid per unit of time, x, y, and z are the three directions into which the fluid propagate, $-U\frac{\partial C}{\partial x}$ is the molecular flow of diffusion of the fluid in the direction considered which is proportional to the gradient of concentration, U is the molecular coefficient of diffusion of the fluid (m^2 s^{-1}), $k_x\frac{\partial C}{\partial x}$ is the flow of diffusion by turbulence of the fluid, k_x is the coefficient of diffusion by turbulence of the fluid (m^2 s^{-1}), and S (Bq kg^{-1} s^{-1}) is the elementary matter concentration exchanged the fluid.

The environment being made up various compartments, this equation is brought back to the equation of diffusion hereafter, particularly in the case of radioactive contamination:

$$\frac{\partial C_i}{\partial t}=D_i^m\Delta C_i+\sigma_i \quad (3)$$

where m is the radionuclide diffused in the medium Iodine (I), which is one of the compartments of our model. In this equation, $\frac{\partial C_i}{\partial t}$ (Bq kg^{-1} s^{-1}) is the variation of concentration of the chemical element in compartment i per unit of time, D_i^m (m^2 s^{-1}) is the coefficient of diffusion of the chemical element m in compartment i, C_i (Bq kg^{-1}) is the concentration of the chemical element m in compartment i, ΔC_i (Bq kg^{-1} m^{-2}) is the divergence of the gradient of concentration of the chemical element in compartment i, σ_i, and (Bq kg^{-1} s^{-1}) is the elementary matter concentration exchanged by i.

(b) Biological accumulation in plants

Radionuclides can enter the lowest trophic level by numerous processes. In terrestrial systems, these include direct adsorption to plant surfaces followed by foliar uptake, direct uptake via stomata (in the case of radionuclides that are present in volatile forms, such as ^{14}C or Tritium) and more importantly for the majority of radionuclides via root uptake (or direct absorption) from soil pore water. The transfer of many radionuclides from soil to plant is accordingly strongly influenced by the general physical and chemical characteristics of the soil. In aquatic environment, Marine algae do not have roots, but do have 'holdfasts' that serve to anchor them to the substrate. Radionuclides are therefore either adsorbed or absorbed directly from the water. However, rates of inter-compartmental transport vary with the radionuclides, the nature and activities of the biota, and properties of the ecosystem. Irrespective of biological necessity, plants have been observed to take up many cations present in their root region. Primordial radionuclides are no exception due to the presence of monazite sands in the study area. In the soil, each radioactive element follows complex dynamics in which a part of its concentration is transported into the soil solution, while another part gradually becomes strongly bound to the soil particles (Zehnder et al. 1996). The portion of these radionuclides which is in the soil solution can be incorporated via the root into the plants. In some cases (U and Th), this is facilitated by their chemical similarity with other elements that the plant normally uses for its growth. It is important to study their dynamics in soil and their transfer to plants as these are basic links in evaluating the transport of these radionuclides along the food chain. To quantify the transfer of a radionuclide from soil to plant, we generally use the corresponding transfer coefficient obtained as the ratio between the activities of the radionuclides under consideration in the said compartment.

3.2 A Few Case Studies

(a) Case of Ra-226, Th-232, and K-40 in various parts of the Alfalfa plant in Egypt

The distribution of naturally occurring Ra-226, Th-232, and K-40 in different parts of the alfalfa plant from two different soils from Qena (South Valley University and Qena Governorate Farms) was studied under natural field conditions. Sixty-two samples (alfalfa plant and its soil) were taken from nine sites inside farms. The results showed that Ra-226, Th-232, and K-40 concentration were found in alfalfa. The distribution of Ra-226 and Th-232 in different parts of the alfalfa plant showed a decreasing trend in root > stem > leaves in that order, while K-40 a decreasing trend in the order stem > leaves > root (Hegazy et al. 2011).

(b) Case of other radionuclides and heavy metals at Chernobyl in Ukraine

After the Chernobyl accident, a vast expanse contaminated with radionuclides of cesium (Cs), strontium (Sr), and plutonium (Pu) radionuclides, also with some heavy metals such as Pb and Cd. Accordingly, clearing such vast contaminated territories by usual engineering methods seems to be improbable or impossible. The results of the study of the possibility of applying phytosorption method to remedy the contaminated soils were presented. A number of soil additives including activated carbon, mineral adsorbents, its modified forms, and composite materials were tested for their influence of ^{137}Cs transition in plants such as sunflower, rape, lupine, amaranthus, mustard, and Jerusalem artichoke. The influence of sorbent type, its amount, and degree of soil activity on the process of soil decontamination was studied. Field experiments were carried out on the ^{137}Cs-contaminated soil, whose radioactivity level ranged from 24 to 0.9 kBq kg^{-1}. Field investigations showed an extraordinary role of sorbents in the migration of radionuclides in the soil–plant-complicated system. It was revealed that in the presence of mineral sorbent, the accumulation of ^{137}Cs by plant only slightly exceeds the natural process of phytoextraction, while the use of composite carbonmineral sorbents essentially increased Cs concentration in plant green mass. Such an effect was observed at the different activity of the soils. It was established that the carbonmineral sorbent into the soil increased the growth of shoots and harvest as a whole. This is probably caused by the presence of some microelements in the sorbent matrix and also by the sorbents' ability to free the soil of herbicide and pesticide contamination, which hampered the plants' growth and development. Simultaneously, the effect of decreasing migration of radionuclides in the plants and essential decreasing of vegetative mass in comparison with the control were also observed. Moreover, this effect is observed in the soils in which some sorbents and complexions can strongly fix radionuclides. This means that it is possible to produce environmentally clean agricultural produce on polluted soils by using the linking function of sorbents or complexions against radionuclides. During the test of a number of radio-accumulating plants, it was found that amaranthus has the highest potential (^{137}Cs) for extracting radionuclides from the contaminated soils. This is due to first of all its naturally high-specific radio-accumulative ability ($k_1 = 1.5$–2.5) and secondly its high productivity ($k_2 = 2.5$–3.5). The introduction of sorbent increased both of these properties ($k_3 = 6$–8) of amaranthus, making possible to use this plant to remove Cs from the soil (Strelko et al. 2000).

(c) Absorption and transportation of molybdenum inside the plants

Mo is an essential element for the higher plants and is a composite element of molybdoenzymes such as nitrate reductase, aldehyde oxidase, xanthine dehydrogenase (XDH), and oxidase sulfites. The lack of Mo in the substrate is lethal for the higher plants. The mechanisms that control the transport of molybdenum in plants and in higher organisms remain unknown. Today, Mo transport systems have been identified and characterized only at the Prokaryotes and some Eukaryotes inferiors (Mendel and Hoesch 2002). However, there are similarities in the physiological answers to molybdenum between the prokaryotic and eukaryotic systems in particular the interaction close with transport to sulfate which is an anion of the same size like molybdate and the obviousness conclude that studies carried out on prokaryotes suggest that the systems of transport and channels of the anion selenites can transport molybdate (Kaiser et al. 2005).

(d) Technetium in the soil and plant

In cultivated soils, the oxide form of technetium ^{99}TcO^{4-} is very mobile. It is accumulated in the leaves especially in the cells containing chlorophyll where it is partly reduced and built in certain amino acids found in the chloroplasts. The plants absorb ^{99}Tc in the form of pertechnetate (TcO^{4-}). Root absorption involves passive as well as active processes that are common to other anions such as sulfates, phosphates, selenates, and molybdates.The pertechnetate is mobile in the xylem, quickly transferred to the leaves, and accumulated in the chlorophyll cells. When Tc is absorbed by roots, it moves toward the leaves, without accumulating in the stem. Tc was found in the leaves in the form of TcO^{4-}, the prevalent form (Echevarria et al. 1997; Simonoff et al. 2003).

3.3 Influence of Radionuclides on Plant Growth and Development

In the previous chapter, we found out that radionuclides are found in plants. This finding raises a significant question, namely, what influence exerted on the plants and their development? We are therefore going to discuss their evolution in the various parts of the plants through the experiments carried out on various plants for each radionuclide by several researchers worldwide.

3.3.1 Strontium

Sr is more readily absorbed from the soil by plants than any other main fallout component. In the UK, field crops may absorb 0.03–4 % of the Sr in the soil per year. Absorption may vary one to two orders with soil type or with plant species. Sr uptake appears to be affected only slightly by pH in the range 5.5–8.5, as indicated by absorption from culture solution by pea seedlings. However, at pH of 4.0, uptake was only about 15 % of that at pH 5.5–8.5. This contrasts with the uptake pattern observed for plants growing in the soil where the presence of other ions (especially Ca) have a dominant influence. The ^{90}Sr/Ca ratios for a plant and for the soil in which it is growing are usually about the same, suggesting that, for any one soil. Ca uptake is indicative of Sr uptake. It is well established that Sr and Ca move upward from plant roots and that downward translocation is negligible; hence the observed decrease in Sr/Ca ratio from root to the tissues most remote from the roots indicates that Sr is less mobile than Ca. This effect is not large enough to produce an appreciable difference between the mean ratios for the shoot and for the soil solution around the roots. Sr accumulates in the shoots of plants, particularly in the leaves rather than in the root. In barley, for example, 96 % of added ^{89}Sr accumulated in the shoots after 56 days of growth (Klechkovsky 1957; Nishita et al. 1961; Russell and Newbould 1966; Russell 1966a, b).

3.3.2 Cesium

In culture solution, Cs may be taken up by plant roots more readily than Sr, but in mineral soil, absorption is low because of the high retention of Cs by mineral particles. Uptake may vary six- to sevenfold with plant species and fourfold with mineral sod type. Cs is readily mobile in all directions within a plant in contrast to the other radionuclides considered here except perhaps I (Selders and Rediske

1954; Klechkovsky and Gulyakin 1958a, b; Nishita et al. 1961; Fredriksson et al. 1966; Russell 1966a, b). Distribution within the plant varies with plant species, length of experiment, and growth conditions. In pot experiments using a sandy loam soil and lasting one growing season, levels of ^{137}Cs in the leaves of beans and lettuces were almost twice those in the stems; and those in the leaves of radishes and carrots were three to four times those in the roots (Romney et al. 1957). In wheat grown in soil and water cultures over one season, levels of ^{137}Cs in the roots were, respectively, 28 and four times those in the stems (Klechkovsky 1957). However, distribution percentages appeared to be more even. In water culture, for example, 17.0, 38.4, 27.4, and 17.2 % of the ^{137}Cs absorbed occurred in the roots, stems, leaves, chaff, and grain, respectively. A reduction in uptake of Cs by plants as the exchangeable K content of the soil increase has been noted by many workers (Fredriksson et al. 1966). A similar reduction occurs when the residual K increases (Fredriksson 1963). The addition of K to soils reduces ^{137}Cs uptake by plants appreciably only when soils contain low levels of K. Hence, in pot experiments, ^{137}Cs uptake by clover was reduced by addition of K after exchangeable K had been reduced by prolonged cropping (Nishita et al. 1960). Progressive fixation of Cs on soil minerals may explain reduction in uptake by plants in long-term studies. Exchangeable Ca, such as exchangeable K, can reduce uptake of Cs, but its effect is usually smaller than that for K (Fredriksson et al. 1966). Because of its very slow penetration into the soil, Cs is accumulated more by plants with root near the soil surface than by deeper-rooting species (Fredriksson et al. 1966). Christenson and Fowler (1961) found these differences in the depth of the root. Systems in clover, lettuces, and grass can cause uptake of ^{137}Cs from near the soil surface to vary by a factor of 2 to 3 (Birkle et al. 1965).

3.3.3 Ruthenium

Ruthenium (Ru) is usually absorbed from soils by plants less readily than Sr or Cs but more readily than the transuranides or Zr. However, Romney et al. (1957) found a greater uptake than for Sr or Cs with barley on some soils. Uptake may vary by one to two orders of magnitude for the same plant species on different soils or between different plants on the same soil. The chemistry of Ru is complex. The element may occur in several different oxidation states or forms in the soil. The form or state may influence uptake by plants. Beans grown in an Oak Ridge shale soil of pH 4.5–4.9 and watered with effluent containing ^{106}Ru and high nitrate and hence probably containing nitrosyl Ru showed concentration ratios on a dry weight basis of 0.43–20.1 for roots, 0.16–9.8 for stems, and 0.44–15.1 for leaves. Uptakes obtained with the commonly used chloride of ^{106}Ru are invariably much lower. Schulz and Babcock (1974), for example, found mean concentration ratios of 0.0018–0.425 for clover growing in soils varying in organic matter content, cation exchange capacity, and pH. (Auerbach et al. 1957; Klechkovsky and Gulyakin 1958a, b; Nishita et al. 1961; Auerbach and Olson 1963; Essington et al. 1963; Schulz and Babcock 1974).

3.3.4 Zirconium and Niobium

Of the commoner pollutant radionuclides except the transuranides, ^{95}Zr + ^{95}Nb are least readily absorbed by plants. ^{95}Zr + ^{95}Nb accumulate in the roots of plants. ^{95}Zr + ^{95}Nb in roots, leaves, stems, pods, and seeds of pea plants grown in soil cultures produced, respectively, 7.1, 2.3, 2.3, and 0.3 disintegrations sec. Wheat plants in soil and culture solution showed a similar pattern; with uptakes in soil one to more than two orders less than those in culture solution. A total of 82.7 % of the absorbed ^{95}Zr accumulated in the roots. About 99.9 % of the ^{95}Zr absorbed by barley growing in a clay suspension accumulated in the roots (Klechkovsky 1957; Klechkovsky and Gulyakin 1958b; Nishita et al. 1961; Russell 1966a; Jacobson and Overstreet 1948).

3.3.5 The Rare Earth Elements: Cerium, Yttrium, and Promethium

Uptake of cerium (Ce) and other rare earths may vary one to two orders for the same plant species on different soils or different species on the same soil. Absorption by plants is negligible except in acid soils where the elements are less precipitated and more water soluble than in neutral or alkaline soils. Pea seedlings in culture solution absorbed ten times more Ce than Pu at pH 4.0, and 200 times more Ce at pH 4.0 than at pH 7.0. Bean plants in a sandy loam absorbed seven times more Ce at pH 4.6 than at pH 6.0. As for Sr, ^{95}Zr + ^{95}Nb, Ru, and Cs, uptake of Ce is greater in culture solution than in soil. Only one percent of added ^{144}Ce was absorbed by two varieties of rice in a sandy loam poor in organic matter (pH unstated), whereas 40 and 70 % were absorbed by the two varieties in culture solution. Absorbed rare earths tend to accumulate in the roots of plants. Rice grown in flooded soil, in soil at field capacity and in culture solutions, 86.3, 96.4, and 99.5 %, respectively, of the absorbed Ce was found in the roots (Klechkovsky 1957; Romney et al. 1957; Russell 1966a, b; Myttenaere et al. 1967). In beans, tomatoes, and barley grown in a silt loam or in culture solution, only a few percent of the absorbed yttrium (Y) and Ce were found in the shoot. Oxygen concentration in the rooting zone of plants influences the mineral content of plant shoots and in culture solutions. Uptake of Ce and Y by shoots of tomatoes, beans, and barley increased with increasing oxygen concentrations around the roots. However, when the plants were grown in soil, results vary too much to allow generalizations about the effect of oxygen to be made (Birkle et al. 1965).

3.3.6 The transuranides: Neptunium, Plutonium, Americium, and Curium

Uptake of transuranides by plant roots, as indicated by the results of laboratory studies and field survey of contaminated sites, is very low. Concentration ratios vary greatly with plant species, soil, and experimental conditions. The order of uptake by plants Np > Am–Cm > Pu is approximately the inverse of their order of hydrolysis and order of adsorption of their oxidation states to colloids, Pu (IV) > Cm (III) = Am (III) > Np, although this order is temporal because of lack of data for Neptunium (Np), Americium (Am), and Curium (Cm). In one test, wheat (grain) absorbed five times more Pu (III, IV, V, VI) than Am (II and I) from a calcareous fine sandy loam of pH 7.9. ^{238}Pu appears to be more readily taken up or less readily lost by organisms than ^{239}Pu since ^{238}Pu/^{239}Pu ratios in soil, plants, and animals are 0.05, 0.1, and 1.0, respectively, (Bennett 1974; Bulman 1976; Dahlman et al. 1976; Schulz et al. 1976; Hakonson and Johnson 1974). Plant species vary in their ability to absorb transuranides, but generalizations and detailed explanation of the differences appear to be currently impossible because of the complexity of the environmental chemistry involved. Lower plants accumulate many fallout radionuclides including transuranides far more than higher plants, but this difference may be due largely to trapping of particulate material and ion exchange at the plant surface. Levels of Pu in lichens in north temperate latitudes, for example, are one to three orders higher than those in higher plants (Bulman 1976; Miettinen 1976; Holm and Persson 1977).

3.3.7 Iodine

Studies of the uptake and retention of radioiodine by plants have concentrated on forage plants and leafy vegetables resulting from aerial deposition. The form in which I occurs in the soil is important. In pot experiments with ryegrass in a sandy loam, elemental I and iodide were absorbed to similar extents (Whitehead 1975). Iodate was taken up much more readily than iodide or elemental I except where organic matter was added as a treatment. The latter addition markedly reduced uptake of all three forms of I. Addition of chalk, which raised the pH to 7.3, led to a marked reduction in uptake of iodide, but a marked increase in uptake of iodate. Katalymov and Churbanov (1960) found that liming decreased the uptake of ^{127}I and ^{131}I by oats, grass, and lettuce in pot and field experiments. Uptake of ^{127}I and ^{131}I by bush beans in culture solution or by barley in soil was reduced about four times when the pH was raised from 4 to 7, apparently because of an effect on the root surface (Selders and Rediske 1954). Changes in uptake of I with pH may be associated partly with changes in solubility particularly when the I occurs as iodate, and partly with effects of I compound on the plants, as in the case of iodide (Whitehead 1975). Except in one study, a pot experiment involving fertilizer application, chloride, which may be added to soil in fertilizers and marine sources, appears not to decrease I uptake by plants (Katalymov and Churbanov 1960; Whitehead 1973). Uptake of I may vary with plant species. I content may vary over one order of magnitude for the same plant type growing on different soils, but I contents of plant and soil or I content and soil type are uncorrelated. This lack of correlation is not surprising in light of the large number of factors μ, which influence the I content of plants (Hanson 1963; Shacklette and Cuthbert 1967).

4 Impact of Radionuclides on Hormones and Enzymes

We saw how absorption of radionuclides happens, their becoming and intervention in the plant through their uptake in its various compartments in a general way. In the same impetus, we shall see how they also intervene at the level of these hormones and enzymes by taking the case of certain radionuclides in the plants.

4.1 Biology of Molybdenum Cofactor (Moco)

Concentrations of Mo in the environment are generally weak. From bacteria to mammals, molybdenum is crucial for their survival. Enzymes that use distinctive chemistry redox of this metal are involved in several metabolic reactions in the carbon, nitrogen, and sulfide cycles. For it to be available for these reactions, the molybdate anions that are soluble in water must be dependent and transported from the environment to the cell and handled so that their chemical properties are made use of in the appropriate context (Hunter 2004).

More than 50 enzymes are known to contain Mo. The majority of them are bacteria, whereas for plants only four are found, that is, nitrate reductase, nitrogenase, and xanthine dehydrogenase–aldehyde oxidase. Those characterized by molybdenum cofactor is part of the active sites of all the molybdoenzymes except the nitrogenase. Molybdenum cofactor consists of a molybdopterin, a pyranopterin phosphorylate with an ene-dithiolate which contains molybdenum. Molybdenum cofactor (Moco) as a catalytic center plays a significant role in the cycles of carbon and sulphurizes and nitrogenizes it. In plants, the protein Cnxl multi-fields catalyzes the insertion of molybdenum in the molybdoptérine (Kuper et al. 2004; Mendel 2007). Among the vegetable molybdoenzymes: XDH and XDH are key enzymes in the degradation of pure oxides in which the hypoxanthine with the xanthine and of the xanthine to the uric acid by simultaneous release of electrons starting from the substrate. XDH is in activity like homodimer of two pennies identical units (150 kDa for the monomer), each one being subdivided in three distinct fields: a field of N-terminal with a size of 20 kDa, a field of 40 kDa, and a C-terminal necessary for the connection and dimerization of Moco. XDH at the plants also has an activity NADH oxidase and so can have additional physiological functions in the metabolism of reactive oxygen because of an increase in the activities of XDH and simultaneously the production of ROS were observed at the time of the plant–pathogenic interactions, in the event of hydrous stress, and in the event of senescence. The aldehyde oxidase (AO): enzymes are very similar to the XDH enzymes as they share a high degree of homologous sequences. They have almost the same molecular mass, bind the same cofactors, form dimers, and also act as a hydroxylases. Enzymes AO can be aligned over their whole length with enzymes of XDH, and the phylogenetic analysis proved that proteins AO derived from XDH after ancient gene duplications. Enzymes AO are the strict oxidases which cannot bind NAD^+ and exclusively employ molecular oxygen-like acceptor of electron, thus producing hydrogen peroxide. An isoform AO (AAO_3) acts better with aldehyde abscisic-like a substrate. The aldehyde abscisic is the native precursor of the vegetable hormone, the acid abscisic which is essential for many processes of development as well as for a series of answers to the abiotic and biotic stresses. The nitrate reductase: The cofactor nucleotidic with molybdenum was discovered at the origin in a mutantnit-1 of Neurospora fouled. Its nitrate reductase had no action, but a mixture of components with a low molecular mass could reactivate it. The mutants of this type often have multiple defects on the level of the various enzymes now indexed like molybdoenzymes. The nitrate reductase is part of these (Pelmont 2005; Mendel 2007).

4.2 Cadmium and Plants

Cadmium is an element that is not necessary for plants and is highly toxic. Its toxicity is considered to be 2 to 20 times higher than that of other heavy metals and, for Pahlsson (1989), it is the fourth most toxic metal for vascular plants. However, the sensitivity with regard to cadmium varies according to the species and even cultivars of the same species (Inouhe et al. 1994; Das et al. 1997; Kuldeep and Brar 2002; Fodor 2002; Lindberg and Greger 2002). Cadmium, unlike transition metals such as iron and copper, do not take part directly in the production of reactive species of oxygen (ROS), namely by reactions of Peg wood and Haber-Weiss. However, it is a metal highly reagent which stimulates the formation of the ROS, leading to the development of an oxidative stress secondary (Siedlecka and Krupa 2002).The ROS are indeed able to oxidize the thiols groups of proteins, thus affecting the activity of many enzymes but also to cause the peroxidation of the lipids, leading to a deterioration of the functions of membranes (Benavides et al. 2005; Dietz 2005). Moreover, modification by the cadmium of composition of phospholipids of the membranes also contributes to the modification of their properties (Olmos et al. 2003; Romero et al. 2004; Fodor 2002).

4.3 Case Study

A recent study has been undertaken by Cerne et al. (2011) in the uranium mine of Žirovski vrh in Slovenia. His goal was to study phytoremediation of a uranium-bearing zone using two families of the plants that is Brassicaceae and Poaceae, which were identified as being hyperaccumulative of radionuclides. The strategy of the study was to use a reed Phragmites australis, which is a watery macrophyte common with these two families of plants close to the dwellings, has a high growth rate and absorbs much metal from the contaminated soils. For that 200 plants of a reed Phragmites australis were planted on two study sites of Boršt and Jazbec;

where their growth was observed. At the beginning of the experiment, the concentrations of the activity (Bq g^{-1} dry weight) of each radionuclide investigated in the soils are measured before the cultivation of the plants. After a certain growth of the plants, the leaves and the stems of an average of 20 specimens were taken each time to be analyzed by alpha and gamma spectrometry. The following results have been obtained:

The results indicated a possible radio-accumulating ability of a common reed grown on a deposit U-mill tailings. Although it is known that lead ions hardly accumulate in the plant tissues, specific physiological characteristics of common reed could influence a higher content of ^{210}Pb in the leaves. On the other hand, low content of uranium in the leaves and stems may be connected to not bioavailable form of uranium in the deposit tailings. The stem has a transport function and translocates nutrients to different tissues. Thus, the presence of small amounts of radionuclides in the stems is logical. Higher potassium content in the deposit tailings could be related to higher potassium content in the uranium ore, and it was obviously not in bioavailable form as potassium in the marsh soil of control site, where one or two orders of magnitude higher activity concentrations of potassium were measured in the plants. The accumulation properties of common reed could be useful in phytoremediation of mine waters or for bioindication of radionuclides in such waters. However, the specific location of ^{226}Ra and ^{210}Pb in the plant tissues of common reed should be further investigated. High-activity concentrations of radionuclides in the U-mill tailings did not negatively impact on plants growth. This means that common reed belongs to the metal-resistant plants with a metal-tolerance mechanism against toxic elements.

5 Conclusion

In this chapter, there was some discussion about the impact of the radionuclides on plants growth, i.e., how these can bring a positive contribution for some and a negative contribution for others on their growth. With this intention, we showed how the radionuclides were absorbed by the plant and their influence in the various compartments of the plant during its growth. We also accessed the action of these radionuclides on the behavior of enzymes and plants hormones. However, it should be noted that the roots, leaves, and fruits of the plants absorb radionuclides most. This varies from one radionuclide to another, and the reactions which take place in these parts depend on the plant type. We can conclude that the radionuclides interfere in the growth of the plants; some of these plants can be used for the decontamination of soils (soils contaminated either by the radionuclides or by metals) by using the various methods of phytoremediation. Phytoremediation appears to be the most prominent and least cost method used for the decontamination of soils.

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Remediation of Radionuclide-Contaminated Sites Using Plant Litter Decomposition

Jörg Schaller, Mohammad Nassour and Carsten Brackhage

Abstract Radionuclide contamination of ecosystems is a commonly known problem for many sites. A frequently used option in dealing with such contamination is phytoremediation. But when thinking of phytoextraction measures, the process of radionuclide enrichment in plant material is not terminated at the end of the growing season, but may increase during decomposition of the litter afterwards. We show that the process of litter decomposition may be mostly important in remediation of radionuclide-contaminated sites for both aquatic and terrestrial ecosystems. Radionuclide concentrations within organic soil/sediment layers increase strongly during decomposition in terrestrial ecosystems as well as in aquatic systems of temperate zones although there are large differences. This is attributed to emerging fixation sites where differences in aquatic and terrestrial systems are dependent on the particular chemistry (e.g. redox chemistry) of the radionuclides. The potentially high accumulation in developing layers of organic matter on the soils/sediments of aquatic/terrestrial ecosystem can easily be removed from the contaminated sites by removing the organic matter. In summary, beside autochthonous processes (e.g. phytoremediation), especially allochthonous processes (e.g. litter decomposition) are very important for the remediation of radionuclide-contaminated sites.

Keywords Biosorption · Carbon turnover · Decay · Ecosystem engineers · Fixation · Litter processing · Organic matter · Radioactivity

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Contents

1 Introduction

Radionuclide contamination of soils and sediments is known for many different ecosystems in many different countries. Apart from radionuclide-rich bedrock (Barth et al. 1998), main sources of radionuclides in the environment are mining activities and industrial waste. Radionuclides may either be drained into hitherto uncontaminated ecosystems or transported even long distances by dust thereby polluting soils and sediments (Entry et al. 1999; Meinrath et al. 1999; Jakubick and Kahnt 2002; Thabayneh and Jazzar 2013).

Phytoremediation would be an option in dealing with such contamination. It comprises techniques that are used especially on sites with comparably low levels of contamination (Salt et al. 1998). As gentle remediation for even larger areas, it became an intensively used technique all over the world (Tripathi et al. 2007) and still is subject to many associated projects on the extension of its operating possibilities/capabilities. For inorganic contaminants like radionuclides, plants in the course of remediation may be used primarily for phytostabilization, rhizofiltration or phytoextraction. The latter result either in a species-dependent accumulation pattern or may even result in phytovolatilization mainly when contaminants like arsenic are methylated (Zhao et al. 2009). Because the accumulation potential is quite different between plants, they have been grouped into species with very high (hyperaccumulators), moderate (accumulators) and no accumulation potential (mainly excluders) (Salt et al. 1998). In any case, this is not only species but also element and site-specific. For radionuclides, the accumulation pattern is not different between different isotopes of the same element. Therefore, the following chapters refer mostly to the element rather than different isotopes. Hyperaccumulating plants of radionuclides have not been described so far. Nonetheless, the accumulation potential of some plant species for uranium led to their use in ore prospection (Cannon 1960). Using the accumulative potential of plants may partially reduce radionuclide concentrations in soils and to a minor extent in sediments (phytoextraction) but without harvest this organically fixed portion cycles back to the soil/sediment via litter fall.

The process of radionuclide enrichment in plant material is not terminated at the end of the growing season, but may increase during decomposition of the litter afterwards (Schaller et al. 2010b, 2011b). More than 80 % of the plant biomass produced in terrestrial ecosystems is directly proceeding to detritus (Gessner et al. 2010). Litter decomposition generally proceeds in three distinct temporal stages of leaching, microbial conditioning and fragmentation (Berg and McClaugherty 2008; Gessner et al. 2010). During the primary decomposition by microorganisms, dissolved organic carbon (DOC) emerges from the litter and microorganisms form together with their exudates a heterotrophic biofilm (Kominkova et al. 2000; Berg and McClaugherty 2008). After the formation of this heterotrophic biofilm (including heterotrophic fungi and bacteria), the litter will be microbially decomposed. In the last step of the decomposition process, the litter will be processed/decomposed/fed on by higher trophic levels (vertebrate and invertebrate animals) (Berg and McClaugherty 2008; Gessner et al. 2010). The fixation and hence the remediation potential for radionuclides therefore are not only given by the accumulation potential of living plants but also by their biomass production and its reformation in the course of decomposition with emerging fixation sites.

This book chapter therefore tries to elucidate the interplay between decomposition of dead plant material (litter) and radionuclide fixation/remobilization potential in aquatic and terrestrial ecosystems and its importance for phytostabilization.

2 Radionuclide Fixation During Litter Decomposition Within Aquatic Ecosystems

On a continental scale not regarding oceans, terrestrial ecosystems may be more important for radionuclide fixation/turnover compared to aquatic ecosystems. But the interplay between organisms and litter in the course of decomposition and hence their importance for radionuclide fixation/turnover may be easily explained for aquatic ecosystems.

The first step during litter decomposition in aquatic ecosystems is the leaching process (Fig. 1). Leaching of DOC as a substantial part herein is mainly occurring during the first 24 h (Gessner et al. 1999). The type of DOC and hence its composition depends on the decomposition stage of the litter and the litter quality. At first, water-soluble fractions (e.g. sugars, amino acids) are released. In a later stage in the course of humification, humic and fulvic acids are leached (Schumacher et al. 2006). These humic and fulvic acids enhance the remobilization of elements from the sediment (Franke et al. 2000). A main part of elements in the so-called dissolved fraction is bound in colloidal form (Baalousha et al. 2006; van Leeuwen and Buffle 2009). In contrast to the above-mentioned findings of DOC impact on element mobilization, other studies found no correlation between an increasing DOC level and the remobilization of radionuclides (Schaller et al. 2008, 2010b). The leaching of radionuclides from the litter (especially litter originating from accumulating plants) is low at the beginning and negligible over the entire time of

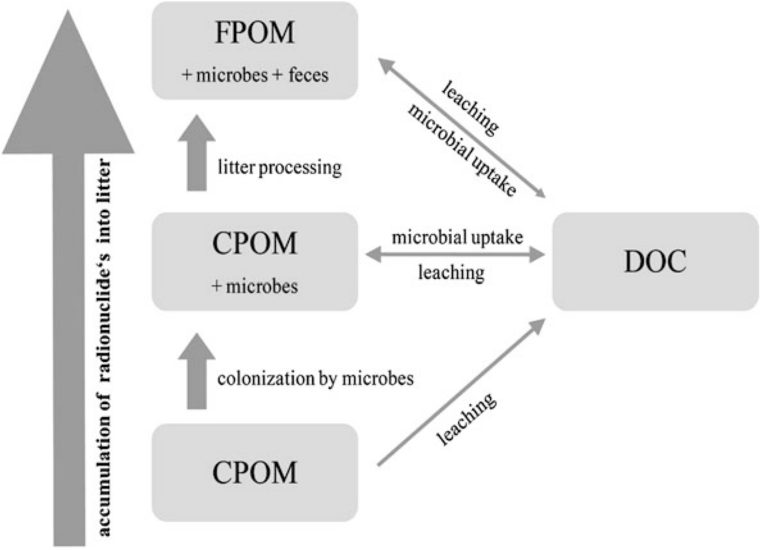

Fig. 1 The process of litter decomposition from coarse particulate organic matter (*CPOM*) to fine particulate organic matter (*FPOM*) and dissolved organic carbon (*DOC*), whereas the resulting changes in litter properties affect the radionuclide fixation, modified after Schaller et al. (2011b)

the decomposition process in relation to the high elemental load of the water passing by during decomposition.

In the second step of decomposition, plant litter will be colonized by microbes (Dang et al. 2007) (Fig. 1). Microbial litter decomposition depends primarily on fungal decomposer and litter diversity (Dang et al. 2005), bacteria and detritivores (Hieber and Gessner 2002), but also on litter quality. Main parameters affecting litter quality are lignin, cellulose, poly-phenol, tannin, nitrogen and phosphorus content (Gessner and Chauvet 1994). But also environmental factors such as pH are important (Lecerf et al. 2007). Decomposition rates of plant litter also depend on water chemistry like acidification (Dangles et al. 2004) and nutrient concentration (Suberkropp and Chauvet 1995). Metals and metalloids themselves affect the microbial decomposer community and consequently affect the decomposition rate (Berg et al. 1991). The amount of fungi growing on the litter decreases in the presence of high radionuclide concentrations (Ferreira et al. 2010). Consequently, the decomposition rate decreases in environments with high radionuclide loads compared to environments with lower radionuclide concentrations, as shown for other elements (Sridhar et al. 2001; Duarte et al. 2008). It was also suggested that microbes produce more exopolysaccharides (EPS) to protect themselves against high concentrations of contaminants (Pirog 1997). These EPS are well known to immobilize elements in high amounts (Huang et al. 2000) by their functional groups and expanded surface area. On the other hand, microbes themselves

Table 1 Activity concentrations shown for ^{238}U, ^{235}U, ^{226}Ra, ^{210}Pb and ^{137}Cs for leaf litter after 8 weeks of microbial decomposition within a stream affected by former uranium mining (Neuensalz, Germany)

Isotope	Activity concentrations (mean ± SD in Bq kg^{-1})
^{238}U	8,300 ± 1,100
^{235}U	390 ± 50
^{226}Ra	650 ± 50
^{210}Pb	<112
^{137}Cs	<5

accumulate high amounts of radionuclides (D'Souza et al. 2006; Purchase et al. 2009). The resulting changes in chemical properties lead to high amounts of radionuclide fixation into plant litter (Flemming et al. 1996; Schaller et al. 2008, 2010b) (see Table 1). The heterotrophic organisms of the biofilm are consumers of oxygen, which results in a redox gradient within the biofilm. There are positive redox conditions at the surface of the biofilm, while negative redox conditions develop towards the centre of the biofilm (thickness 100–1,000 μM) (Paerl and Pinckney 1996). But the negative redox potential formed by heterotrophic biofilms can be inverted in the presence of high concentrations of manganese oxidizing the biofilm (Chinni et al. 2008), which in turn leads to a remobilization of radionuclides with reverse redox chemistry (e.g. uranium) (Schaller et al. 2010b). In contrast, in the absence of high amounts of manganese, it was revealed that high amounts of radionuclides (e.g. lead and uranium) are fixed by these heterotrophic biofilms (with negative redox potential) attached to plant litter (Schaller et al. 2008).

The fragmentation of plant litter depends on the feeding activity and behaviour of animals like invertebrates (Graça 2001). The preferred food of, for instance, invertebrate shredders as key species in aquatic litter decomposition is plant litter colonized by microbes in the primary stages of decay (full established biofilm) (Graça et al. 2001; Franken et al. 2007). These invertebrate shredders cut the litter into smaller particles, which increases the surface area (Schaller et al. 2010a; Schaller and Machill 2012). On this enhanced surface area, more microbial biofilm will grow, which significantly increases the fixation capacity for elements (Schaller et al. 2010a) (Fig. 1). An effect of invertebrate shredders on contaminated leaf litter was first described for uranium (Schaller et al. 2008). It was found that high uranium concentrations in water and litter have no negative effect on the survival rate of invertebrates (Schaller et al. 2009). In contrast, a significant lower decay rate of leaf litter in metal-polluted compared to unpolluted environments was found by experiments with shredding invertebrates (Medeiros et al. 2008), depending on different element speciation and pH values (Schaller et al. 2008). Furthermore, invertebrate shredder shows a lower feeding rate in radionuclide-polluted environments compared to uncontaminated environments (Goncalves et al. 2011). Data from an in situ experiment revealed that invertebrate shredders facilitate radionuclide (e.g. lead) enrichment into smaller particle sizes of POM in

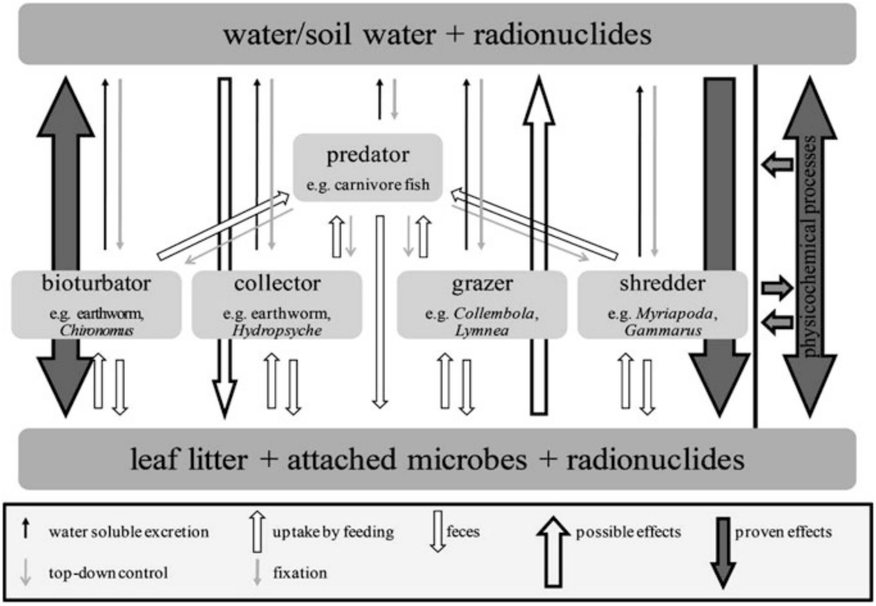

Fig. 2 Overview of proven and possible effects of different types of functional animal groups on metal/metalloid accumulation/remobilization within terrestrial/aquatic ecosystems, modified after Schaller et al. (2011b)

the presence of high concentrations of DOC (Schaller et al. 2010b). These high DOC levels were expected to bind radionuclides (Sachs et al. 2007), but the opposite was shown in different experiments (Schaller et al. 2010b). Current studies reveal a control of radionuclide fixation by silicon availability during plant growth reducing the binding sites at the litter surface for plant material grown under high silicon availability (Schaller 2013), forming a so-called silicon double layer within the epidermis near area (Schaller et al. 2013a). This seems to be quite important because of the enhanced decomposition rate of this plant litter (probably more biofilm) with high silicon content (Schaller and Struyf 2013). The role of other important ecosystem processes has still to be elucidated (see Fig. 2). For some chironomids, it is known that they have a positive effect on radionuclide remobilization (Schaller 2014), but less is known about the effect of other keystone species so far. Hence, a broad area of research opens here. Altogether, the developing layers of organic matter on/in aquatic sediments have a very high potential to trap radionuclides during organic matter decomposition. Hereafter, radionuclides can be easily removed from contaminated sites by removing the organic matter.

3 Fixation Potential of Terrestrial Ecosystems and the Influence of Litter Decomposition

The fixation potential of terrestrial ecosystems such as grasslands or forests is highly dependent on soil organic layers and therefore influenced to a great extent not only by the accumulation potential of abundant plant species resulting in contaminated litter but also by litter decomposition affected in turn by emissions of radionuclides. Terrestrial ecosystems are more complex compared to aquatic systems regarding litter decomposition. The complexity is based on spatial and temporal heterogeneity of the soil texture resulting in a high density of different habitats. This leads to a more or less simultaneous occurrence of leaching, microbial decomposition, fragmentation and decomposition by animals (Berg and McClaugherty 2008). In many cases, fallout radionuclides were investigated for their mobility in different soils and soil layers. This was done with a compartment model using the activity concentrations over time for the different soil layers resulting in residence half-times (e.g. Bunzl et al. 1994). It was shown that long-lived radionuclides such as $^{239+240}$Pu, ^{241}Am and ^{137}Cs are still found within a 30 cm depth of a grassland soil after 30 years of deposition (Bunzl et al. 1994). Residence half-times were found not to be significantly different for all three radionuclides, but derived migration rates taking into account the thickness of each soil layer are increased with depth. Further investigations showed that especially organic matter is involved in the fixation potential and hence low migration rates in upper soil layers (Bunzl and Trautmannsheimer 1999). Rafferty et al. (2000) summarize the migration mechanisms and hence the pools and pathways for ^{137}Cs in a coniferous forest soil. They propose a three-phase model where the phases are discrete but may occur in a given area in parallel. In the first phase, ^{137}Cs is intercepted by the forest canopy and washed onto the soil and a portion of 20–40 % immediately percolates through the organic layers into the underlying mineral soil. Over the next estimated 5 years, the remaining ^{137}Cs moves by leaching and/or decomposition from the Ol- and Of-horizons to the Oh-horizon, where here in the third phase, it is more or less permanently fixed. This is due to a very slow decomposition of organic matter in the Oh-horizon of coniferous forest soils.

A leaching of radionuclides from the plant litter coincidently to the mobilization of DOC may probably take place if the concentration of the fresh fallen plant litter is very high (Sauras et al. 1994). Vice versa plant litter may accumulate radionuclides from soil water/splashing water during litter decomposition as was shown for ^{137}Cs. During plant growth on contaminated soils, the radionuclides will accumulate within the soil organic layer due to plant uptake and even more during litter decomposition afterwards (Choppin 1988; Tikhomirov and Shcheglov 1994; Fesenko et al. 2001). The radionuclide accumulation/fixation by plant litter during decomposition in terrestrial systems takes place as described for aquatic systems (see above). Such an accumulation of radionuclides in litter during decomposition was described for many other ecosystems (Agapkina et al. 1995; Bunzl et al. 1998;

Copplestone et al. 2000; Vaca et al. 2001), where it was indicated that the radionuclides are bound organically (Virchenko and Agapkina 1993). If the soils of terrestrial ecosystems develop such a layer of organic matter and trap the radionuclides within this layer during decomposition, the radionuclides can be easily removed from the contaminated sites by removing the layer of organic matter.

Unfortunately, organic matter is transported from the litter layer into the mineral soils, mostly by soil fauna (Chamberlain et al. 2006; Frelich et al. 2006). This mixing of organic matter with the soil mineral phase is in turn a process diminishing remediation options for radionuclides. In contrast to predicted effects of the soil fauna, such a radionuclide transport into deeper soil horizons was found only in very low amounts (Bunzl et al. 1992). The assemblage of the soil fauna changes during decomposition. For larger detritivores, the litter transformer or shredder such as isopodes, millipedes and epigeic earthworms feed earlier on the organic matter (detritus) than soil-dwelling animals (bioturbation) such as endogenic earthworms, insect larvae and some collembolans (Bastow 2012). Hence, the detritivores feeding first transforming the litter into smaller particles (shredder) lead to an enhanced fixation of radionuclides to organic matter (litter under decomposition), by extending the surface area of the litter, as shown earlier for aquatic systems (see above). In contrast, detritivores following after these first processes affect the radionuclide fixation and distribution by bioturbation (see above).

In conclusion, radionuclide concentrations within organic soil layers may increase even strongly during decomposition in terrestrial ecosystems, as shown earlier for aquatic systems. But this depends on factors such as type of radionuclide, bedrock concentrations, emissions, plant community, climate conditions and hence development of organic layers. In temperate zones, litter decomposition and organic soil formation following phytoremediation by planting accumulating species can be highly complementary for remediation of radionuclides. This combination has the potential to increase the effectiveness of remediation measures of radionuclide-contaminated sites tremendously. Autochthonous processes (e.g. phytoremediation during plant growth) and allochthonous processes (e.g. litter decomposition) together are probably more efficient in element fixation/immobilization as has been indicated already for aquatic ecosystems (Schaller et al. 2013b).

4 Radionuclide Impact on Higher Trophic Levels

There is a general trend that organisms in a contaminated environment show increased concentrations of the contaminants (Rainbow 2002). Hence, concentrations of radionuclides well above background levels may affect multiple levels of biological organization from ecosystem, community, population, individual, cellular, subcellular to molecular levels (Peplow and Edmonds 2005). Effects of stressors on the food web are described to be dampen at higher trophic levels in the course of transfer to the food web (Schindler 1990), but can also be intensified (Breitburg et al. 1999). Still, bioaccumulation differs depending on species (Cain et al. 2004), age (Wallace et al. 2003), sex and fitness of the animals. The uptake of potential toxic trace elements can take place via two different pathways: either directly via surface and/or via ingestion and uptake in the digestive tract (De Schamphelaere et al. 2004). Regulation of potential toxic trace element uptake includes one of the following adaptive strategies: (1) limiting entrance into the body directly, (2) balancing uptake by increasing excretion thereby maintaining a constant total concentration or (3) by detoxifying and storing elements when entering organs or cells (e.g. metallothioneins) (Barka et al. 2010). Some invertebrates show only a low accumulation potential presumably excluding uptake which has been explained by the detoxification of potential toxic elements in gastrointestinal epithelial cells and excretion together with these epithelial cells (Ahearn et al. 1999; Amiard et al. 2006). A higher accumulation of radionuclides into the gut system compared to the remaining tissues of the body was shown for species of the genera *Gammarus* (Sola and Prat 2006; Schaller et al. 2011c). Also potential toxic elements/radionuclides adsorb onto the chitin cuticle of invertebrates (Lenhart et al. 1997) depending on cuticle properties (Lightner et al. 1995). Thereby, a size-dependent bioaccumulation of elements on the surface of invertebrates was observed (Wang and Zauke 2004) resulting in an increased tolerance. Some invertebrates living in environments with high element load may be able to excrete ingested elements to clean their body and avoid high internal concentrations (Tessier et al. 1994; Alves et al. 2009; Schaller et al. 2011c). But many species associated to litter decomposition are described to be highly sensitive to radionuclides (Borgmann et al. 2005; Sola and Prat 2006). Elements can enter organisms via passive transport across the plasmalemma using carrier systems that yield them to higher affinity sites (S- and N-protein binding). Elements can also enter cells down a concentration gradient through specific hydrophilic transmembrane channels. Passive diffusion may also be a way when being in a lipid-soluble (non-polar) form or elements are taken up by endocytosis (Rainbow 1997). It is therefore unlikely that differences in element accumulation between the gut system and other (remaining) tissue(s) of invertebrates are exclusively due to the prevention of entrance into gut epithelial cells. Dietary uptake of elements into invertebrate shredder may cross into gut epithelial cells from the faeces. However, significant differences in radionuclide concentrations between the gut system (and its content) and remaining tissues (Schaller et al. 2011c) show that effective detoxification mechanisms (like sequestration and/or excretion) exist to prevent their entrance into the haemolymph and subsequent dispersal throughout the body. Within hepatopancreatic cells, dietary non-essential elements are isolated by complexing with metallothioneins, glutathione and inorganic anions including sulphur and phosphorus removing them from metabolic activities and hence reducing the haemolymph concentration (Barka et al. 2001; Chavez-Crooker et al. 2003; Amiard et al. 2006). Non-essential elements are precipitated into sulphur and phosphorus containing granules (Nassiri et al. 2000; Sterling et al. 2007).

These elements are sequestered for the life of the cell and then expelled into the gut system at the end of the cell cycle (Sterling et al. 2007; Barka et al. 2010).

Invertebrate shredders are known from toxicity tests to be sensitive to radionuclides such as uranium (Robertson and Liber 2007). It was shown that mortality increases by increasing pollutant concentration. On the other hand, some populations of the European shredders *Gammarus* sp. show no significant differences in survival rate in experiments between polluted and non-polluted water and food (Schaller et al. 2009, 2011a). Furthermore, for *Tubifex* sp. (Oligochaeta) another litter processing invertebrate, no effect of metals/radionuclides on the survival rate was found (Kaonga et al. 2010). In addition, some collectors of the genus *Hydropsyche* (Trichoptera) seem also not affected by high metal/radionuclide concentrations (Clements et al. 2000). For terrestrial systems, less is known about the toxicity of radionuclides on soil animals. For earthworms and soil arthropods, no effects were detected below 1,000 mg U kg^{-1} (earthworm) and 350 mg U kg^{-1} (soil arthropods) (Sheppard and Stephenson 2012). This very high threshold may indicate an adaption to habitats with high radionuclide load. A biomagnifications (e.g. for invertebrates) was proven (Copplestone et al. 1999) but may be rather explained by the amount of radionuclide containing food and faeces within their body than by a real uptake and accumulation of radionuclides within tissues other than the gut system, as it was found earlier for aquatic detritivores (Schaller et al. 2011c). Interestingly, earthworm and collembola seem to be highly tolerant regarding even radiation (Fuma et al. 2011). With an ED50 of about 1,300 Gy for collembola (Nakamori et al. 2008) and about 800 Gy for earthworms (Fuma et al. 2011), an effect of radiation from radionuclides on soil animals on contaminated sites can be excluded. Hence, effects of radionuclides on health and mortality of animals on contaminated sites are more due to their chemical toxicity.

We suggest that organisms living in habitats which tend to high radionuclide accumulation may have been adapted during their evolution, because they had to handle these conditions the whole time. If they had not be adapted to high radionuclide load (probably by minimizing the uptake or maximizing the excretion), they would not still live in such habitats. Hence, a low mortality rate in the presence of high concentrations of metals/radionuclides in the environment can possibly be explained by the evolutionary adaptation to these environments with high bioavailability of radionuclides/metals.

5 Conclusions

In this chapter, we have seen that the process of litter decomposition can be used to enhance the effectiveness of the remediation of radionuclide-contaminated sites. The litter decomposition and radionuclide accumulation is controlled by microbes (bacteria and fungi), their exudates (e.g. EPS), nutritional properties and higher trophic levels (e.g. shredder, grazer and bioturbator). Litter decomposition in aquatic systems proceeds in three distinct temporal stages of leaching, microbial conditioning and fragmentation. Terrestrial ecosystems are more complex compared to aquatic systems regarding litter decomposition, because of the complexity based on spatial and temporal heterogeneity of the soil texture resulting in a high density of different habitats. This leads to a more or less simultaneous occurrence of leaching, microbial decomposition, fragmentation and decomposition by animals in terrestrial systems. The most important process for radionuclide accumulation/fixation is the formation of the heterotrophic biofilm by the microbial decomposer community. These biofilms have a very high capability for radionuclide accumulation/fixation. Within these biofilms growing on plant material/organic matter, the radionuclides can be enriched up to ore level. The impact of higher trophic levels in turn controls the radionuclide accumulation/fixation by influencing the amount of heterotrophic biofilm growing on the litter (e.g. invertebrate shredders) or changing the redox conditions (e.g. bioturbators). Altogether, litter decomposition is highly prone for remediation of radionuclide-contaminated sites, because of the very high capability of radionuclide accumulation/fixation of litter/organic matter under decomposition. We suggest that the remediation of radionuclide-contaminated sites will be much more efficient with the implementation of litter decomposition into the phytoremediation techniques compared to techniques without litter decomposition.

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Bioaccumulation of Radionuclide Metals in Plants: A Case Study of Cesium

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Abstract Phytoremediation is a new and fast-developing technology with non-destructive properties and ideal for removal of heavy metals and radionuclides from industrial effluents. Many plant species have high efficiency for adsorption and uptake of cations including heavy metals and radionuclides from contaminated soil and water. Plant screening and selection for remediation purposes is considered an important and a major step for implication of this technique. Taking into account geological characteristics and climatic conditions of a particular geographic area, most suitable plant species must be selected and implemented to achieve high rates of remediation. In this study, three plant species (*Amaranthus chlorostachys* var. Chlorostachys, *Calendula alata* Rech. F., Fl. Iranica, and *Chenopodium album*) were studied with the objectives to evaluate their potential for uptake of cesium from wastewater containing cesium salt. At the first step, plant seeds were selected and grew in hydroponic system using “Hoagland” solution. “Hoagland” solution is a standard medium made from distilled water enriched with specified nutrients for plant growth studies. After 2 months, plants were incubated in solutions with three different concentrations of stable cesium. The first set of experiments were carried out using four containers including a control solution containing distilled water free of Cs, and three other distilled water solutions containing 0.5, 2, and 5 mg l^{-1} of CsCl, respectively. In the second set of experiments, standard Hoagland solution was used. *A. chlorostachys* and *C. album* plants were placed in containers filled with Hoagland medium mixed

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with equal volume of cesium solution made from dissolving CsCl in distilled water, so that the final concentration of CsCl was 1 mg l^{-1} in first container and 2.5 mg l^{-1} in the second. For each set of experiments, several similar containers were used to ensure validity of results. Experiments were arranged in randomized block design for a period of 15 days. Then, *C. album* that showed to be an effective accumulator of cesium was selected for anatomical studies. After separation, aerial organs (stem, leaf) of *C. album* plant were laid in a solution of alcohol and glycerin for fixation and anatomical investigations. The concentration of cesium in the growth solution, (Hoagland diluted with distilled water containing cesium), and in plants (dried and digested in acid) was measured by atomic absorption spectrophotometry (Varian Spectra AA-55B). The results of the present study showed that *A. chlorostachys* remediated 65 ± 4.11 % of cesium from simulated wastewater. Efficiency of *C. alata* in phytoremediation of cesium chloride (5 mg l^{-1}) and Hoagland medium was 89.35 ± 0.25 %. Comparison of plants remediation potentials showed higher efficiency of *A. chlorostachys* while in bioaccumulation potential comparison, *A. chlorostachys* showed higher efficiency. Anatomical changes studies of *C. album* plants showed that important change was increase in crystals (entering cesium to crystalline structure) quantity in stem parenchyma and their color embrace, due to cesium uptake. This tolerant plant converted cesium ions to crystals molecules in shoots. Plants grew healthy in contaminated environments and the remediation efficiency of cesium reached close to 90 % in *C. alata* when cesium salt concentration was 2.5 mg l^{-1} and Hoagland solution was used. It was concluded that in a proper culturing condition, all these plants are tolerant to radionuclides and could be suitable candidates for remediation of radionuclide wastes. Consequently, it was proved that phytoremediation could be a complimentary treatment technique for removal of radionuclides from waste discharges at nuclear sites.

Keywords Phytoremediation · Cesium · Plant species · Solution

Contents

1 Introduction

The development of nuclear energy power plants and the use of radio nuclides for many industrial, medical, and also research projects could cause major radionuclide contamination of the environment and may result in health problems for several decades if no special remediation is undertaken (Vandenhove 2013). Although various technologies for remediation of contaminated soil, sludge, sediment, surface water, groundwater, and wastewater have been used, they are usually very expensive and have secondary impacts on the environment. In case of water and wastewater, the efficiency of remediation and cost-effectiveness are major considerations to strategy formulations (Salt et al. 1998; Eapen et al. 2006; Zhang et al. 2007; Chakraborty et al. 2007; Singh et al. 2008). Phytoremediation is a new and fast-developing technology with nondestructive properties and ideal for managing this type of effluents. Many plant species have been identified as hyperaccumulators; that is, they have the ability to accumulate high concentrations of metals, without impact on their growth and development (Xiong 1997). Many studies have examined the ability of plants to remediate a variety of elements from diverse media. The achievement of phytoremediation depends on plant growth rate and obtaining high metal concentrations in plant shoots (Alloway et al. 1990; Tanhan et al. 2007). Plants uptake system is defined as a system that involves ions uptake from environment. The main components of the species-specific uptake system are transporters and channels (Maestri et al. 2010). Depending on the plants uptake rate and distribution of elements within the plant organs, their content and distribution is significantly diversified (Verkleij and Schat 1990). Moreover, plant concentrations of metals may be influenced by a variety of conditions. Not only pH but also other ions concentrations and environmental conditions may interact with uptake of elements and sometimes change the growth rate of plants (Massas et al. 2010). In recent studies, there seems to be an enduring interest in selecting native plants that are tolerant to pollutants and many researchers have evaluated the phytoremediation potential of native plants under field conditions (McGrath and Zhao 2003). Experimental real-life studies are necessary and may have to include a range of contaminant concentrations, mixtures of various contaminants, and different experimental treatments to prove the sustainability of this technique for efficient remediation. Plant selection is based on growth rate, contaminant translocation, accumulation potential, and tolerance to contaminants. Singh et al. (2009) have found that plants belonging to Chenopodiaceae, Amaranthaceae, and Asteraceae families are effective remediators of many cations including heavy metals. The main purpose of this work has been largely to evaluate the potential of

Chenopodium album, *Amaranthus chlorostachys*, and *Calendula alata* to phytoremediate stable cesium as an analog of radioactive Cs. Moreover, metal concentration in shoots of plants was compared with those in roots. *C. album*, *A. chlorostachys*, and *C. alata* are fast-growing plants that grow on wide geographic allocations in arid and semiarid regions of the world. Many of plant species have a high efficiency in radionuclide uptake from polluted environment (McCutcheon and Schnoor 2003; Dabbagh et al. 2008). Radionuclide's bioaccumulation potential is different in various plants. Some plants that have been used for this purpose are shown in Table 1. Plant screening and selection for remediation purposes is the most important step of this method. Based on geographical and climatic characteristic of each area, plant species can be selected and used.

Radionuclides occur naturally in soil. A radionuclide is described as an atom with an unstable nucleus. When radionuclides decay, they produce ionizing radiation. Radioactive substances decay with a characteristic "half-life," which is described as the time required for reducing the activity of a radioactive particle to half of its initial activity. Those resources that produce radiation over long periods have adverse effects on human health. The main categories of ionizing radiation emitted as a consequence of radioactive decay are alpha, beta, gamma, radiation, and fission with emission of fragments and neutrons. Radioactive decay can neither be inhibited nor accelerated. Since half-lives can be many thousands or millions of years, radionuclides must be safely stored meanwhile. While radionuclides appear physically in the environment, those categorized as injurious are usually of anthropogenic sources, or enhanced by human activities and dispersed through industrial applications. The Nuclear Regulatory Commission classified radioactive materials into two categories: high-level and low-level classes. High-level radioactive substances mainly originates from the fuel used by a reactor to produce electricity, while low-level wastes include material that either has a short decay time or has become contaminated with or activated by nuclear materials. Uranium mining and nuclear reactors are common sources of radionuclide production. The processing of uranium in nuclear reactors similarly produces isotopes such as cesium 137 and strontium 90, which take a considerable long time to decay. In addition, uranium 238 decays to form radium 226 that has a half-life of 1,600 years. A lot of these radioisotopes stay active in industrial by-products and wastes for long periods of time. Other usually encountered radionuclides include cobalt 60, plutonium, radium, radon, technetium 99, thorium, and uranium. Radionuclides are used for a variety of purposes that can be highly beneficial or equally high health hazards if disposed and discharged inefficiently. Radionuclides are useful for their chemical properties and are used in biomedicine in the diagnosis, treatment, and research into diseases. Radionuclides that release gamma rays can be used as tracers to monitor bodily states and the functioning of organs, while radium and radon can be used in the treatment of cancerous tumors. Furthermore, in scientific research into genetics, radionuclides allow researchers to label molecules and study processes such as DNA replication, and transformation.

Table 1 Candidate plants used for phytoremediation of radionuclides

Plant (scientific name) or family or genus	English name
Cs	
Acer rubrum, Acer pseudoplatanus	Red maple
Agrostis spp.	Bent grass
Amaranthus retroflexus	Red-root Amaranthus
Amaranthus chlorostachys	Red-root Amaranthus
Brassicaceae	Mustards, mustard flowers, crucifers, or cabbage family
Brassica juncea	Indian mustard
Cerastium fontanum	Big chickweed
Beta vulgaris, *Chenopodiaceae*	Beet, Quinoa, Russian thistle
Cocosnucifera	Coconut palm
Eichhornia crassipes	Water hyacinth
Eragrostis bahiensis (*Eragrostis*)	Bahia love grass
Eucalyptus tereticornis	Forest red gum
Festuca arundinacea	Tall fescue
Festuca rubra	Fescue
Helianthus annuus	Sunflower
Larix deciduas	Larch
Liquidambar styraciflua	American sweet gum
Liriodendron tulipifera	Tulip tree
Lolium multiflorum	Italian ryegrass
Lolium perenne	Perennial ryegrass
Panicum virgatum	Switch grass
Phaseolus acutifolius	Tepary beans
Phalarisarundinacea L.	Reed canary grass
Picea abies	Spruce
Pinus radiata, *Pinus ponderosa*	Monterey pine, Ponderosa pine
Sorghum halepense	Johnson grass
Trifolium repens	White clover
Zea mays	Corn
Sorghum	Sorghum
Fagopyrum esculentum	Buckwheat
Chromolaena odorata	Siam weed
Beta Vulgaris	Beet
Salsola kali	Prickly saltwort
Caloptropisgiantea	Sodom apple
Phlox hoodii	Spiny phlox
Purshia *tridentate*	Antelope brush
Artemisia vulgaris	Mugwort
Eriogonum umbellatum	Polygonaceae
Lomatium foeniculaceum	Sulfur flower buckwheat

(continued)

Table 1 (continued)

Plant (scientific name) or family or genus	English name
Castilleja angustifolia	Northwestern Indian paintbrush and desert Indian paintbrush
Taraxacum officinale	Common dandelion
Eichhornia crassipes	Water hyacinth
Cordylanthus ramosus	Bushy bird's beak
Co	
Haumaniastrum robertii	Copper flower
Thlaspicae rulescens	Alpine pennycress
Acer rubrum	Red maple
Thlaspicae rulescens	Alpine pennycress
Pu	
Liquidambar styraciflua	American sweet gum
Liriodendron tulipifera	Tulip tree
Ra	
Poaceae various spcies	
Dryopteris scottii	
Asteraceae various species	
Sr	
Acer rubrum	Red maple
Brassicaceae	Mustards, mustard flowers, crucifers or, cabbage family
Beta vulgaris, Salsola Kali	Beet, Quinoa, Russian thistle
Eichhornia crassipes	Water hyacinth
Eucalyptus tereticornis	Forest redgum
Helianthus annuus	Sunflower
Liquidambar styraciflua	American sweet gum
Liriodendron tulipifera	Tulip tree
Loliumm ultiflorum	Italian ryegrass
Pinus radiata, *Pinus ponderosa*	Monterey pine, Ponderosa pine
Apiaceae (*a.k.a.Umbelliferae*)	Carrot or parsley family
Fabaceae (*a.k.a.Leguminosae*)	Legume, pea, or bean family
Vetriveria zizanoides	Vetiver, Khas–Khas
U	
Amaranthus	
Brassica juncea	Brown mustard
Brassica chinensis	Bok choy
Brassica narinosa	Tatsoi
Eichhornia crassipes	Water Hyacinth
Helianthus annuus	Sunflower
Juniperus	Juniper
Picea mariana	Black spruce
Quercus	Oak
Salsola kali	Russian thistle (tumble weed)

(continued)

Table 1 (continued)

Plant (scientific name) or family or genus	English name
Salix viminalis	Common Osier
Silene vulgaris(a.k.a. Silene cucubalus)	Bladder campion
Zea mays	Maize
Helianthus annuus	Sunflower
Brassica juncea	Mustard greens, Indian mustard, Chinese mustard, or Leaf mustard
Ti	
Phlox hoodi Plemoniaceae	Spiny phlox or carpet phlox
Eriogonum polygonaceae	California buckwheat
Cordylanthus capitatus	Clustered bird's beak
Antennaria	Cats foot
Chaenactis, *Asteraceae*	
Fabaceae	
Microsteris gracilis Polemoniaceae	Slender phlox

Another major usage of radionuclides, specifically the element uranium, is for energy production. Interest in Cs distribution in plants and the movement of this element in ecosystems extends back to the 1950s by the development of nuclear technologies used for energy production (Cook et al. 2007). Release of cesium nuclides in environment may be very similar to other more hazardous radionuclides present in wastes from nuclear wastes. The radioisotopes of cesium (^{134}Cs and ^{137}Cs) may be of special concern because of their similar behavior to the necessary element "K" in plants, their solubility in aquatic ecosystems, the volatilization, release and dispersal in major reactor accidents, and the great quantity and persistence of ^{137}Cs in spent fuel and reprocessed wastes (Pipíska et al. 2004; Pinder III et al. 2006). According to studies carried out by Tsukada et al. (2002) and Vinichuk et al. (2010), strong correlations exist between distribution of ^{137}Cs and stable Cs in plants. Moreover, Soudek et al. (2006) did not find any differences between the uptake of radioactive and stable Cs isotopes by *Helianthus annuus* L. Stable Cs is phytotoxic in solutions exceeding 200 mM (Borghei et al. 2011).

2 Methodology

Three plant species (*A. Chlorostachys*, *C. alata* Rech. F., Fl. Iranica, and *C. album*) were used to evaluate their potential for phytoremediation of Cs solutions and their tolerance to cesium uptake. Healthy seeds of *A. chlorostachys*, *C. alata*, and *C. album* were surface sterilized by 1 % sodium hypochlorite for 20 min. *C. alata* seeds were sown in a substrate containing perlite and vermiculite 3:1 (v/v) moistened with distilled water for 4 weeks until seedlings with two leaf pairs were established. *A. chlorostachys* and *C. album* seeds were germinated in sand. Then, one-month-old plantlets were transplanted in plastic trays containing 10 l nutrient solutions. The composition of macro-elements per 100 l solution was as follows: 100 ml $NH_4H_2PO_4$ (115 g l^{-1}); 600 ml KNO_3 (107 g l^{-1}); 400 ml Ca $(NO_3)_2.4H_2O$ (236 g l^{-1}); 200 ml $MgSO_4.7H_2O$ (246 g l^{-1}); 150 ml Fe-EDTA (5 g l^{-1}). The composition of microelements (100 ml of solution all together) also was: H_3BO_3 (0.38 g l^{-1}); $ZnSO_4.7H_20$ (0.22 g l^{-1}); $MnSO_4.4H_2O$ (1.02 g l^{-1}); $CuSO_4.5H_2O$ (0.08 g l^{-1}); $(NH_4)6Mo_7O_{24}.4H_2O$ (0.02 g l^{-1}). Solution pH was adjusted to 5.5 through 5.8 with 0.1 M NaOH or 0.1 M HNO_3 and continuously aerated with an air pump for proper mixing and oxygenation of the solution. Nutrient solutions renewed at every tenth day. Level of the solutions in trays was made up with nutrient solution when required. Each tray contained 24 plants. Plants were grown outdoors with temperature ranging from 31 °C through 40 °C (maximum daily temperature) and 17 °C through 28 °C (minimum daily temperature) with natural light during the experiment. After 4 weeks, plantlets with uniform size were selected and transferred to 1-l flasks.

2.1 Experiments Using Hydroponically Grown Plants

2.1.1 Remediation of Cs Solutions Contaminated with Cs

The roots of cultured plants were washed thoroughly with distilled water, and plants were incubated with roots immersed in 1 l solution with three different Cs concentrations. The treatment samples included: (1) control sample free of Cs, samples 2, 3, and 4 containing 0.5, 2, and 5 mg l^{-1} of CsCl, respectively. Consequently, the concentration of Cs ions in the solutions was 0.47, 1.58, and 3.95 mg l^{-1}. The experiment was arranged with each treatment in triplicate samples. The treatment group was exposed to CsCl solution for a period of 15 days in 1,500-ml flasks. pH of the solution was adjusted to 5.5. The average root lengths were 300 mm (*C. alata*), 350 mm (*A. chlorostachys*), and 200 mm (*C. album*). Those for plants shoots were 350 mm (*C. alata*), 400 mm (*A. chlorostachys*), and 300 mm (*C. album*). *C. alata* and *A. chlorostachys* plants had a massive root system. Each flask contained three plants, which represented one replicate. Plants grown in water served as control samples. Distilled water was used for solution preparation and for makeup of lost water. After treatment period, samples of solutions were drawn out from the solutions and analyzed for Cs concentrations. In all experiments, Cs contents of solutions were determined using atomic absorption spectrophotometry (Varian Spectra AA-55B).

2.2 The Percentage Metal Uptake

The percentage metal uptake was calculated.

$$\% \text{ uptake} = [(C_0 - C_1)/C_0] \times 100$$

where C_0 and C_1 are initial and remaining concentrations of metal, respectively, in solution (mg l^{-1}) (Abdel-Halim et al. 2003; Tanhan et al. 2007).

2.3 Distribution of Cs in *Calendula alata*, *Amaranthus chlorostachys*, and *Chenopodium album*

At the end of the experiment, plants were thoroughly washed with distilled water, separated into root and shoot and dried in an oven at 60 °C for 48 h. The dried samples were digested in HNO_3:$HClO_4$ (5:1, V/V) and analyzed for Cs by flame atomic absorption spectrophotometry. The concentrations of elements in the samples are reported on a dry matter basis.

2.4 Concentration Ratio

The concentration ratio (CR), defined as the ratio of metal concentrations in plant shoots to those in the roots (Gonzaga et al. 2006; Bidar et al. 2007), was calculated to check the effectiveness of plants in translocating metals to their aerial parts (Dahmani-Muller et al. 2000; Zabudowska et al. 2009).

2.5 Statistical Analysis

The experiments were performed in triplicate, and the statistical analysis was performed using statistical analysis system (SAS) software package. To confirm the variability of results, all the data were subjected to analysis of variance to consider the significance differences. More over, mean comparison between data was obtained using Duncan's test.

2.6 Anatomical Studies

After separation, aerial organs (stem, leaf) of *C. album* plant were laid in alcohol and glycerin for fixation. After a period of seven days, a handy section was prepared and colored with multiple coloration (Carmen Zuji and methylene blue with ratio 1:10). Then, samples were photographed and investigated by Nikon microscope.

2.7 Result and Discussion

Methods for cleaning up radioactive contaminated environments are urgently needed (Vinichuk et al. 2013). Phytoremediation technique is based on the capability of various plants to remove different hazardous contaminants present in the environment.

2.8 Cs Remediation from Different Solution Using Hydroponically Grown Solution

As a result of this study, it was found that the selected plants were efficient in remediation of Cs from Cs wastes (Table 2) with different rates.

In the other experiments, when *A. chlorostachys* and *C. alata* plants were exposed to 0.5 mg l^{-1} CsCl solution, the remediation percent was calculated equal to 45 ± 8.59 and 46 ± 2.12, respectively. Moreover, when *C. album* plants were incubated in CsCl solution in three different concentrations of 0.5, 2, and 5 mg l^{-1}, the remediation percent was 68 ± 2.12, 39 ± 3.48, and 52 ± 5.57, respectively. Mean comparison analysis in remediation potential of these three plant genotypes was shown in Fig. 1. As shown in Fig. 1, *C. album* and *A. chlorostachys* had a similar behavior in cesium uptake. As presented in this study, weeds potential for phytoremediation was more than ornamental plants. Weeds were tolerant to Cs wastes. Moreover, *C. album* plants showed high potential of remediation of CsCl solution; it was selected for anatomical studies.

2.9 Cs Concentration Ratio

Cs CR in different plants was calculated in Table 3. Plants potential for phytoremediation can be assessed by CR index. In phytoextraction, radionuclide ions transfer from roots to shoots. So, plants shoots can be harvested. Tolerant plants limit movement of metals from the environment to shoots and from shoots to roots. Consequently, bioaccumulation in these plants is low. Hyperaccumulators actively uptake metals ions and transport them to their shoots. In the present study, most of the plants due to CR more than 1 are proper for cesium phytoremediation purposes. In this study, *C. alata* plants showed highest CR equal to 4.98 ± 0.04 as a

Table 2 Plant remediation potential of Cs wastes

Cs	*Amaranthus chlorostachys*	*Amaranthus chlorostachys*	*Calendula alata*	*Calendula alata*
Concentration in initial cesium solution (mg l^{-1})	1.58	3.95	1.58	3.95
Concentration in cesium solution after remediation period (mg l^{-1})	54 ± 0.06	2.30 ± 0.15	0.92 ± 0.02	1.89 ± 0.04
Remediation (%)	65 ± 4.11	41 ± 3.92	41 ± 1.59	52 ± 1.02
Concentration in initial cesium and Hoagland solution (mg l^{-1})	7.9	19.75	7.9	19.75
Concentration in cesium and Hoagland solution after remediation period (mg l^{-1})	0.90 ± 0.01	3.01 ± 0.03	1.66 ± 0.02	2.10 ± 0.05
Remediation (%)	88.56 ± 0.19	84.72 ± 0.15	78.98 ± 0.25	89.35 ± 0.25

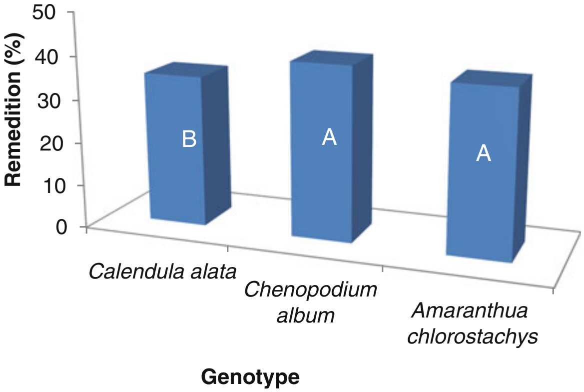

Fig. 1 Mean comparison analysis in remediation potential of different plant genotypes

result could be used for remediation of radionuclide wastes. Concentration ratio of *C. album* during phytoremediation of Cs waste was 3.33 ± 0.03 that was more than 1 and could be account as suitable candidate. Sandeep and Manjaiah (2008) found ^{134}Cs transfer factor to straw and grain decreased significantly with increase in K application levels. The ^{134}Cs uptake was highest in spinach followed by mustard, gram, and wheat crops. The weighted transfer factor values (straw plus grain) to spinach, mustard, and gram were experimented to be 5.54, 4.38, and 2.20 times higher as compared to wheat crop.

2.10 Anatomical Changes

Anatomical structure of aerial organs during phytoremediation process and accumulation of cesium was changed. These changes increased when cesium

Table 3 Concentration ratio (CR) of cesium through plants in different cesium chloride solutions

Cesium (mg kg^{-1})	Concentration ratio (CR)								
	Amaranthus chlorostachys			*Chenopodium album*			*Calendula alata*		
	0.47	1.58	3.95	0.47	1.58	3.95	0.47	1.58	3.95
	1.76 ± 0.01	1.07 ± 0.03	2.19 ± 0.05	1.06 ± 0.05	1.19 ± 0.02	3.33 ± 0.03	0.47 ± 0.04	2.84 ± 0.06	4.89 ± 0.04

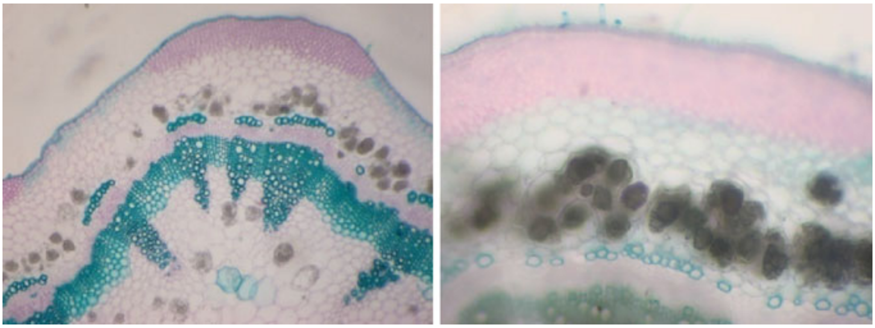

Fig. 2 Increase of crystals quantity in stem parenchyma and their color embrace after remediation of 5 g l^{-1} cesium chloride

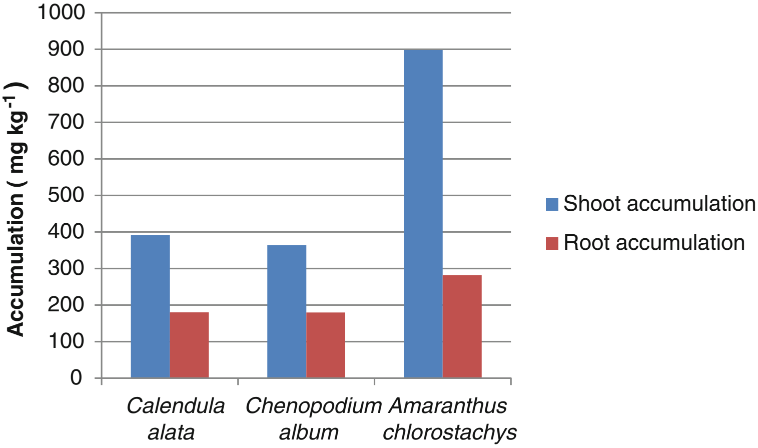

Fig. 3 Mean comparison analysis of accumulation potential between different plant genotypes

concentration in waste water intensified. As shown in Fig. 2, the most important change was increase of crystals quantity in stem parenchyma and their color embrace. The number and variation of the plant species and communities in polluted sites seemed most closely related to the activities of radioactive material and the pH value of the environment (Hu et al. 2014). In a study carried by Hu et al. 2014, the plant species in the sampling sites with moderately low activities of ^{226}Ra and relatively high pH value showed a comparatively stable vegetation community. In our previous study, Cs accumulation in plant was studied (Moogouei et al. 2011), and further to past results, the plant accumulation potential was compared. As shown in Fig. 3, different plant genotype had significant different in phytoremediation. So, plant screening studies and experiments are important steps of using this technology. *A. chlorostachys* plants showed higher potential for cesium accumulation compared with *C. alata* and *C. album.* As shown in Fig. 4,

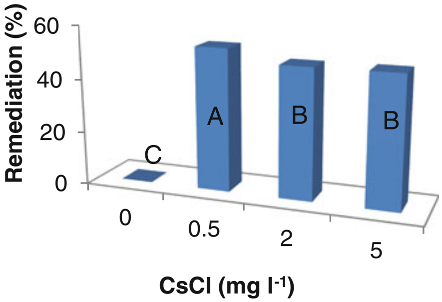

Fig. 4 Mean comparison analysis of Cs remediation potentials of plants in 4 different Cs concentrations

phytoremediation techniques are more efficient in lower concentration of radionuclides such as Cs. As shown in Fig. 5, more accumulation occurred during the absence of more Cs ions in the environment. Cs has unknown vital biological role for plant (Saleh 2012) while due to similarity between chemical characteristics of cesium and potassium, plants uptake both of them through one mechanism. Many transporting proteins (low affinity, inward-rectifying K channel, nonspecific, voltage insensitive cation channel, high affinity $K^+ - H^+$ symporter, voltage-dependent Ca^{2+} channels, and outward-rectifying cation channels) make possible penetration of Cs^+ across the cell membranes in plants (Bystrzejewska-Piotrowska and Bazala 2008). Furthermore, pH and temperature were important factors controlling the phytoremediation efficiency. Saleh (2012) found that the uptake rate of radiocesium from the simulated waste solution by *Eichhornia crassipes* plant is inversely relative to the initial activity content and directly relative to the increase in mass of *Eichhornia crassipes* plant and sunlight exposure, while in the present study, increase in Cs ions in solution increased Cs uptake and accumulation in plants. Moreover, as explained in Saleh (2012), research uptake rate and translocation factor were more in plants with higher mass. The uptake efficiency of ^{137}Cs present with ^{60}Co (cobalt is one of the essential trace elements necessary for plant) in mixed solution was higher than if it was incubated separately. In our study also, the presence of macro- and micronutrient ions in solution significantly enhanced remediation efficiency. Based on Saleh (2012) studies, sunlight was the most required factor for the plant vitality, growth, and radiation resistance. In the study carried by Singh et al. (2008), Vetiver grass (*Vetiveria zizanoides*) L. Nash plantlets when experienced for their potential to remove ^{90}Sr and ^{137}Cs (5×10^3 k Bq l^{-1}) from solutions spiked with individual radionuclide showed that 94 % of ^{90}Sr and 61 % of ^{137}Cs could be removed from solutions after a period of 7 days. In this study and in case of ^{137}Cs, accumulation occurred more in roots than shoots. In contrary, in our study, in all three plant species, accumulation was more in shoot than root with a significant translocation factor. When experiments were performed to study the effect of analogous elements, K^+ ions reduced the uptake of ^{137}Cs, while ^{90}Sr accumulation was found to decrease in the presence of Ca^{2+} ions in *V. zizanoides* plants. In contrary, in *A. chlorostachys* and *C. alata* plants tested in this research, the presence of K^+ increased uptake of Cs from solution. Plants of

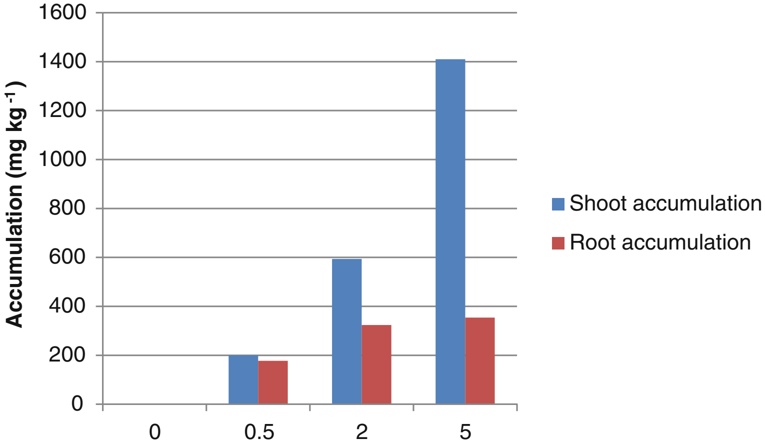

Fig. 5 Mean comparison analysis of accumulation potential through plants in 4 different Cs concentrations

V. zizanoides could also efficiently remediate radioactive elements from low-level nuclear waste, and the level of radioactivity was reduced below detection limit at the end of 15 days of exposure. As discussed by Singh (2008), *V. zizanoides* may be a potential candidate plant for phytoremediation of ^{90}Sr and ^{137}Cs. We can conclude that higher remediation potential could be achieved when using *C. alata* and *A. chlorostachys* for radionuclide phytoremediation purposes. Wang et al. (2012) had found that the ^{88}Sr and ^{133}Cs transfer factor values were 1.16–1.72 and 0.24–0.60, respectively, in *Raphanus sativus* L. plants. In that study, the highest ^{88}Sr accumulation was 239.18 μg g^{-1} dw, while, the highest ^{133}Cs accumulation was 151.74 μg g^{-1} dw in soil polluted with 40 mg kg^{-1} ^{88}Sr. The lowest ^{88}Sr accumulation was 131.03 μg g^{-1} dw and the lowest ^{133}Cs accumulation was 12.85 μg g^{-1} dw when the concentration of ^{88}Sr in the soil was 5 mg kg^{-1}. As there was minute influence of high concentration of ^{88}Sr on the total biomass of plants, therefore, the radish is one of the ideal phytoremediation candidate plants for Sr-polluted soils. In our study also, tested concentrations of Cs ions have no significant influence in total biomass of plants. These plants also showed higher CR. Li et al. (2013) have found that epiphytic *Tillandsia* plants are efficient air pollution biomonitors and usually used to monitor atmospheric heavy metal pollution, but rarely nuclides monitoring. So, they evaluated the potential of *Tillandsia usneoides* for monitoring ^{133}Cs and investigated whether Cs was trapped by the plant external surface structures. The results obtained from this study showed that *T. usneoides* was tolerant to high Cs stress. As presented in our study, they discussed that with the enhancement of Cs solution concentration, the total of Cs in plants increased significantly, which suggests that the plants could accumulate Cs quickly and effectively. Consequently, *T. usneoides* has significant potential for monitoring Cs-polluted environments. Our study showed that weeds such as *C. album* and

Fig. 6 *Amaranthus chlorostachys* plants grown in Hoagland and CsCl solution

A. chlorostachys and *A. retroflexus* were considerable potential for monitoring Cs-polluted environments. In addition, when radionuclides have been accumulated by organisms, their behavior usually reflects their similarities to macro- and micronutrients as well as nonessential elements (Markich and Twining 2012). Metabolic mechanisms moving toward homeostasis naturally make internal organism chemistry less dynamic than that in the external water columns. Many important biotic factors recognized to influence radionuclide bioaccumulation are age, gender, and size. Moreover, there are differences within and between species that reflect the natural variability within any system. These findings led to water ecosystems conservation. Scanning electron microscopy and energy dispersive spectrometer analysis in *Tillandsia usneoides* plants showed that Cs was seen in each type of cells in foliar trichomes, and the ratio of Cs in the internal disk cell was higher than that in ring cell and wing cell, which showed that the mechanism of adsorption Cs in *Tillandsia usneoides* has an active factor (Li et al. 2013). Available observation due to absorbtion and accumulation of Cs in *C. album* in our study classified to five groups includes:

1. Increase of crystals quantity in stem parenchyma and their color embrace.
2. Density of xylem vein groups and reduce of their dimension in stem.
3. Increasing color embrace property of xylem component in stem.
4. Decreasing cutaneous parenchyma in plants under Cs uptake stress.
5. Increasing crystalline density and colored embrace in leaf's parenchyma.

Cooperating Cs in crystal's structure and its accumulation in vacuoles of *C. album* caused plant to absorb more content of Cs radioisotopes from the environment without any serious incurred damage to plant and phytotoxicity effects. Ionic channels are activated ways for transmitting charged ion through cell membrane. Most of these channels are permeable toward some other cations such as sodium, lithium, rubidium, and Cs. Sizes of these cations are between 0.13 to 0.19 nm, which is very similar to potassium's dimension (0.27 nm), and this fact causes their spread through these channels (Tajadod and Moogouei 2012). Investigation on adsorption of Cs in this plant can be carried for air monitoring and phytoremediation of radionuclides. REML modeling of wide-ranging CR/concentration datasets showed that the concentrations in plants of calcium, magnesium, and strontium were notably influenced by phylogeny (Willey 2013). The chemical form of a radionuclide or stable element is commonly of greater biological importance than the total concentration of it in the environment (Markich and Twining 2012). This concept was now being integrated into mechanistic frameworks such as biotic ligand and bioaccumulation models by regulators for protecting freshwater ecosystems.

3 Conclusion

Due to very high health risks, all nuclear sites have efficient systems to control their pollution and avoid environmental contamination. However, as a result of inefficiencies in treatment facilities or accidental discharges, spillage of radioactive effluents is always a cause of concern. To avoid disastrous consequences, further steps must be taken to ensure safety and upgrade preventive measures. For this goal, this study was undertaken to examine the possibility of phytoremediation as a complimentary treatment method for waste discharges from nuclear sites. Phytoremediation can be a good option for areas with low contaminations and represents a suitable and sustainable method of remediation (Willscher et al. 2013). Current research indicated that roots and shoots of *A. chlorostachys* had the most efficiency in bioaccumulation. Moreover, shoot Cs concentration was more than roots resulted in high CR of Cs. As shown in Fig. 6, plants grew healthy in contaminated area. The remediation efficiency of radionuclides reached close to 90 % in *Calendula alata* in 5 mg l^{-1} when Cs salt was introduced into Hoagland solution. So, in a proper culturing condition, all these plants are tolerant to radionuclides and could be proper candidates for remediation of radionuclide wastes.

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Speciation of Actinides After Plant Uptake

G. Geipel and K. Viehweger

Abstract Actinides have high hazardous potential. They are non-essential elements. Besides the natural occurring elements such as uranium, thorium and their decay products, the transuranium elements neptunium, plutonium, americium and curium are important actinide elements to be considered in nuclear waste management and nuclear accidents. It is known that the toxicity of an element depends strongly on its speciation and therefore also on its bioavailability. As an example, the toxicity of uranium decreases in the series uranyl phosphates > uranyl citrates > uranyl carbonates. This underlies the importance of knowledge about the element speciation of actinides. Plants are an important part within the food chain. Therefore, knowledge about the speciation of actinides in these organisms may evince hazards after consumption and ways to protect living beings. Nevertheless, the knowledge about actinide speciation in organisms including plants is very rare. Most of publications up to now deal with transfer factors. A few publications point out that actinides exist often in a phosphate form. Nevertheless, during uptake, other binding forms may play important intermediates. Also, information about binding forms of actinides in storage compartments inside plant cells helps to estimate the hazardous potential. Uranium, americium and curium show luminescence properties, which can be used for the determination of the binding of these elements. Therefore, it can be expected that the knowledge increases in the next decade.

Keyword Actinides · Uranium · Plutonium · Curium · Plants · Cellular uptake

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Contents

1 Introduction

Besides natural occurrence of actinides, uranium and thorium are the most impact having higher actinides in biological systems; it is connected to the release of transuranium elements in nuclear accidents as in Chernobyl and Fukushima and from that scenarios which are seen in the discussion of radioactive waste storage.

In radioactive waste storage sites in the deep underground, however, the first organisms which may have contact to actinides are micro-organism. In later transport to the earth surface, these radionuclides may also access the food chain via several ways of uptake. One of these ways may occur by uptake of actinides by plants. Nevertheless, the uptake depends on the bioavailability of these elements and therefore also on the speciation or binding form before and after uptake. It can be stated already here that some of these radionuclides are much less studied than others. This may be caused by the difficult handling of the radioelements, as they are α-emitting radionuclides, and therefore, special equipment in the laboratories is necessary as well as regulations of radiation protection have to be considered.

An introduction in the uptake of radionuclides by plants has been given by Greger (2004). Besides the description of common uptake mechanisms, only little information about actinides is given. An overview about soil to plant transfer is given by Robertson et al. (2003). The factors vary very strong depending on plant species, soil and experimental conditions, but compared to Sr isotopes, the values for actinides are smaller.

2 Thorium

Thorium occurs only in the tetravalent oxidation state. Therefore, mostly insoluble species were formed under conditions which are relevant for growing of plants.

Soudek et al. (2013) found in their study in tobacco plants that thorium is mostly accumulated by the roots. In this study, also the influence of citric, tartaric and oxalic acid in the hydroponic medium was tested. All these changes of the medium caused an increase of the thorium concentration especially in the roots. The presence of antioxidants such as diamines and polyamines resulted in a decreasing uptake. It was also found that phosphate in the medium is the most important factor for thorium accumulation. Absence of this anion caused a strong increase in the uptake.

Using greenhouse experiments, Shtangeeva et al. (2005) studied the influence of thorium on plant growth of wheat. The information is focussed on effects of plant growth, but concentration of thorium in several plant parts is given. As expected, the roots of 13-day seedlings showed highest Th concentration of about 0.8 mg kg^{-1}, and no difference was found for Th in the soil or if Th was added to germination medium. Leaves did not show any difference if compared to control plants. However, the seeds showed some difference. Highest observed Th content (2.0 mg kg^{-1}) was found in the seeds contacted with the contaminated medium for germination. In a second, newer publication, also uranium was studied besides thorium (Shtangeeva 2010). The results confirm earlier estimations that roots contain higher amounts of the radionuclides than the leaves. This is explained by the function of the roots as barrier against the uptake of non-essential metals. However, other parameters such as soil- and plant-specific properties influence the uptake strongly.

3 Protactinium

Protactinium is a natural occurring radioelement in the uranium and thorium decay series. The isotope ^{231}Pa with a lifetime of 3.25E04y is longest living isotope. However, it is a decay product of ^{235}U that amounts to only 0.7 % of the natural uranium. It can be seen that the influence of this radioelement is very small. Nevertheless, its most important oxidation states are +3, +4 and +5, whereas in the oxidation state, +5 oxocations are formed.

Only a few studies with Pa have been published and deal mainly with the observed oxidation states and speciation (Marquardt et al. 2004).

No references about uptake and speciation in plants in the literature reflect the very rare occurrence of these radionuclides.

4 Uranium

The uptake and effects of uranium in biological systems have been reviewed (Ribera et al. 1996). However, its speciation has not been treated in depth. Instead, sequential extraction techniques have been employed to obtain rough estimates of the species formed.

Sorption of uranium in lichen from aqueous media has been studied by Haas et al. (1998). Highest uptake values were observed in the pH range 4–5. Microanalysis showed that the uranium distribution is heterogenous with high local concentrations in the upper cortex. It should be important to state that the uranium concentration seems to be correlated to the phosphor concentration. As no uptake was studied, the authors conclude that biomass-derived phosphate ligands or functional groups on the surface may be involved.

A general overview on speciation and bioavailability of uranium in aquatic systems can be found by Markich (2002). It is stated that the free uranyl ion UO_2^{2+} and its first hydrolysis product UO_2OH^+ are the major bioavailable forms. Complexes with inorganic or organic ligands (phosphate, carbonate and humic substances) should be less bioavailable. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) is attested as one method to determine the speciation of uranium(VI). However, this viewpoint may be a little bit too easy. One the one hand, as example, uranium forms strong complexes with phosphate, and the solubility of uranyl phosphate species is rather limited. On the other hand, phosphate is an important constituent of the nutrition media. Plants are able to exudate agents to make insoluble components bioavailable. As organic acids form soluble complexes with actinides, the uptake by plants may increase if such species are present in the soil. Plant uptake of uranium was increased in soil containing acetic, malic and citric acid (Huang et al. 1998). The concentration of uranium in shoots from *Brassica juncea* and *B. chinensis* increases from 5 mg kg^{-1} to more than 5,000 mg kg^{-1} when the soil is treated with citric acid. The authors explain this extremely high uptake by the biodegradation of citric acid probably to propionic acid (Huang et al. 1998). However, the nature of these degradation products was usually not determined (Joshi-Tope and Francis 1995; Francis et al. 1992).

A clear intracellular uptake of uranium by algae was stated by Fortin et al. (2004). The intracellular uptake after 30 min shows the same concentration dependence as the “extracellular” adsorption. Citrate and EDTA decreased the uptake. This was also stated for addition of phosphate ions; however, the shown diagram for phosphate addition leads more to the conclusion that phosphate had nearly no influence. A strong correlation between the free uranyl ion in solution and the intracellular uranium concentration was shown. The authors conclude that the mechanism of the cellular uptake occurred via free uranyl ions.

Biosorption and possible accumulation of uranium were investigated in the green algae *Chlorella vulgaris* (Vogel et al. 2010). Thereby, a possible release of cellular compounds such as organic acids during 96 h contact with uranium was discussed. First attempts to identify the metal speciation were done by TRLFS, extended X-ray absorption fine structure (EXAFS) spectroscopy and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Based on the results, the authors stated that the coordination of uranium is mainly influenced by the applied experimental conditions. The metal was preferentially coordinated via carboxylic groups. However, the obtained data clearly indicate the need for a fractionation of cellular compartments prior analysis using the above-mentioned methods.

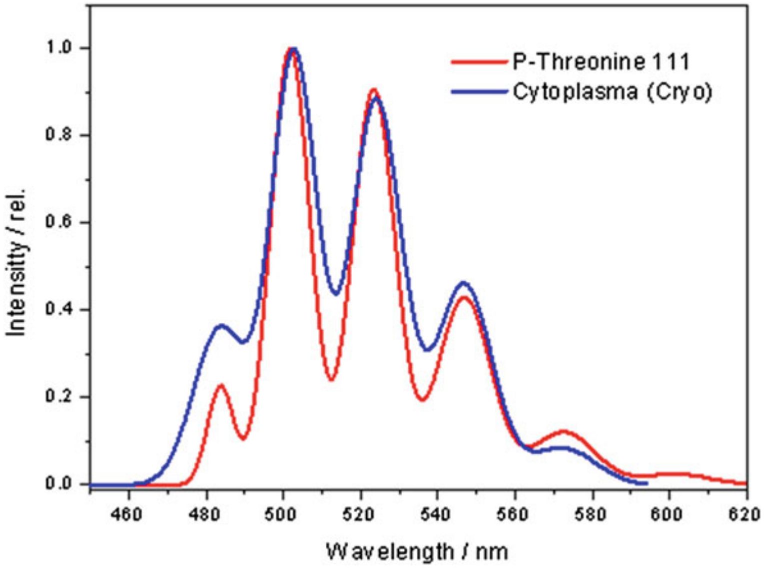

Fig. 1 Luminescence spectrum of uranium(VI) in the cytoplasma fraction at 150 K

A first approach was done with suspension cultures of canola (*Brassica napus*) which were treated with 10 μM uranyl nitrate, and 24 h later, the cells were disrupted and fractionated according a protocol published by Larsson et al. (1994). The uranium speciation in the several cell fractions (plasma membrane fraction, cytoplasma and cell nuclei fraction) was then observed by TRLFS. As example, the luminescence spectrum at 150 K of the cytoplasma fraction is shown in Fig. 1. Comparison of these spectra with databases shows that the assignment of the measured spectra is a complicated process. In the case of cytoplasma, it seems to be somewhat easier, as the spectrum is very comparable to spectra, which were obtained for uranium(VI)—ortho-phospho-L-threonine (Guenther et al. 2006). However, for the other fractions, the assignment is more complicated. Besides the agreement of the localization of the emission bands, other spectral factors as intensity distribution between the several emission bands and the full width at half maximum of a band are important data. Last but not least, also the luminescence lifetime has to be taken into consideration. In case of the shown spectrum, the data set is summarized in Table 1.

Nevertheless, also this comparison gives only first hints to the uranium speciation in the cytoplasma of plant cells. It cannot be excluded that also other species are involved. This can be seen by comparing the data in Table 1, difference in emission bands up to 1.4 nm, FWHM up to 8.9 nm as well as in the area fit. Another drawback of fractionation is the disruption of tissues and cells, and it cannot be excluded that the metal speciation is changed.

Table 1 Comparison of spectral data of uranium(VI) in cytoplasma fraction and uranium(VI)-ortho-phospho-L-threonine

Data	Cytoplasma fraction	Uranium(VI)-ortho-phospho-L-threonine
Emission band/nm	483.7	483.7
	503.2	501.8
	524.3	523.4
	546.3	546.9
	569.7	572.7
Full width at half maximum (FWHM)/nm	16.8	7.9
	13.6	12.0
	15.8	13.1
	17.0	16.3
	20.8	19.0
Area (%)	7.8	5.0
	30.9	33.8
	35.5	33.4
	19.3	19.7
	6.5	6.5

To get insights into the complex coordination chemistry of actinides with biological compounds such as proteins, model complex formations should be characterized. An example for this was the investigation of interactions between aspartyl-rich pentapeptides and actinides(IV) (Jeanson et al. 2009). Adenosine triphosphate (ATP) is formed in mitochondria, and its energy transfer functions are mostly intracellular. The binding of uranium and neptunium to ATP has been examined (Geipel et al. 2000; Rizkalla et al. 1993). Strong dynamic quenching processes are induced upon complex formation, and the decrease in fluorescence intensity can be used for determination of thermodynamic data. The derived stability constants are strongly pH dependent. This indicates that protons are involved in the chemical equilibrium. A formation constant of $\log K_A = -3.80 \pm 0.44$ was found for the 1:1 complex.

Useful tools for the work on a molecular level are antibodies because of their specific targeting. The synthesis of 5-isothiocyanato-1,10-phenanthroline-2,9-dicarboxylic acid (DCP) and its complex with uranyl ions has been reported (Blake et al. 2004). The complex interacts with the polyclonal antibodies 8A11, 10A3 and 12F6 when it is coupled to a carrier protein for injection into mice. Dissociation constants for the respective UO_2(DCP)–antibody complexes were estimated to be 5.5, 2.4 and 0.9 nM. Metal-free DCP is bound to antibodies with lower affinities (by about three orders of magnitude). Comparison with other metal–DCP complexes showed that these three antibodies allow very sensitive detection of UO_2(DCP). It was concluded that such specific uranium-binding capabilities could be pivotal to monitor and control uranium contamination, supporting the concept of developing immunoassays for UO_2^{2+}.

Plant/soil concentration ratios for uranium and thorium have been reviewed already 25 years ago (Sheppard and Evenden 1988). The ratios show a wide variability, depending mainly on factors connected to the soil type and also on the plants used in the studies. Overall, means of 0.0045 for uranium and 0.0036 for thorium were given. Nevertheless, it should be also noticed that the compiled data point to a relationship between the uranium and the phosphorous concentration in the fresh sample. The correlation coefficient seems to be not very strong ($r = 0.75$), but this result should be not neglected, and it is also not in agreement with the conclusion of Markich (2002).

Some basic statements about the concentration ratios were also given:

1. Fine-textured soils have lower concentration ratios than coarse-textured mineral soils.
2. Cereal grain crops show lower values than root crops.
3. The concentration ratios decrease with increasing contaminant concentration.

The uptake of radionuclides by plants results in formation of species other than those present in soil (Mortvedt 1994). This review also concluded that uptake generally depends on the concentration of radionuclides in the soil. Some plants (such as black spruce) contained more uranium than present in the natural background, indicating mechanisms of accumulation (Simon and Ibrahim 1990). However, up to date, no uranium hyperaccumulator (shoot/root ratio <1, Baker 1981) has been identified.

The uptake of elements of the uranium series was studied at a mine mill (Ibrahim and Whicker 1992). The plants growing on weathered tailings showed the highest uptake for uranium followed by thorium. Unfortunately, the data are not comparable to others, because the authors used mixed groups of plants. A detailed compilation about the behaviour of U-238 series radionuclides in plants and soils was published recently by Mitchell et al. (2013).

Many other publications deal with the transfer of actinides from soil to plants, but speciation studies in plants are very rare. The first study dealing with the speciation of uranium during the growth of plants was carried out in 1998 (Ebbs et al. 1998). Pea (*Pisum sativum*) was investigated under a range of conditions. The speciation of uranium in hydroponics solution (modified Johnson's nutrient solution) was modelled with the program GEOCHEM-PC. Plants were pretreated with a phosphate-containing solution without uranium for 10 days. They were then transferred to nutrient solutions without phosphate but including U(VI) ions and grown for an additional seven days before harvesting. The roots and shoots were rinsed and dried before digestion with nitric acid. The uranium uptake was influenced by pH. At pH 5, when uranium was present as the free uranyl cation (UO_2^{2+}), the root concentration was generally higher than that in the shoots. Other species, *Phaseolus acutifolius* and *Beta vulgaris,* showed the highest uranium uptake, but information on the speciation in these plants is not available.

Another investigation of uranium speciation in plants was done in lupines (*Lupinus angustifolius*) (Guenther et al. 2003). Two series of experiments were performed either growing in soil or in hydroponic solution. Speciation was different: uranyl hydroxo species were the major species in hydroponic solution while carbonate species dominated in the soil pore water. However, speciation in several parts of the plant was the same and independent of the species present in the original solution. Uranium is bound mainly to phosphoryl groups in plant compartments, a fact confirmed by EXAFS and TRLFS.

A clear increase in knowledge of uranium speciation in plants was published recently by Laurette et al. (2012). They exposed three plant species [oilseed rape (*Brassica napus*); sunflower (*Helianthus annuus*); and wheat (*Triticum aestivum*)] with different uranyl species at various pH values which led to different patterns of U accumulation in plant roots and translocation to the leaves. Scenario 1 consisted of mainly UO_2^{2+} and carbonate species at pH 4 which resulted in uranium precipitation on root epidermis. However, a low amount of uranium was located in the soluble fraction and could be transported via apoplasm or symplasm. The presence of phosphate in the nutrition medium (scenario 2) caused only a moderate uranium uptake and its translocation was negligible. In contrast, carbonate or citrate amendments at neutral or acid pH (scenario 3) strongly increased uptake to the roots and translocation to the shoots. However, at the moment, it is not clear which speciation of uranium occurred in different plant tissues. An interesting point was the detection of possible uranyl-binding proteins in soluble, cellular fractions separated by sequential extraction followed by gel chromatography. Further work is necessary to identify these proteins and to gain insight in their possible functions. One promising approach is to participate in the emerging field of metallomics and metalloproteomics such as combined sensitive metal detection via inductively coupled plasma mass spectrometry (ICP-MS) with MS-based proteomics methods. Cvetkovic et al. (2010) impressively demonstrated the power of these new set-ups using high-throughput tandem mass spectrometry (HT-MS/MS) and ICP-MS to characterize cytoplasmic metalloproteins from exemplary micro-organisms identifying uranyl-binding proteins. Comprehensive reviews discussing this promising field were published recently by Maret (2010) and Yannone et al. (2012).

To get an idea about metal speciation in plant tissues and cells, working on a molecular level is mandatory. Thereby, plant cell cultures are well-suited models for characterization of possible metal-chelating metabolites, subcellular trafficking and signalling or accumulation. One example using suspension cultures of canola (*Brassica napus*) was shown recently by Viehweger et al. (2011). Thereby, the influence of uranium on the cellular glutathione pool (GSH, reduced form; GS-SG oxidized form) and the resultant consequences for its redox status has been investigated. After cellular uptake, uranium(VI) probably formed cyclic complexes via the carboxylic acid groups of GSH (Frost et al. 2011), whereas uranium(IV) is preferentially coordinated at the sulfhydryl moiety as it was postulated for cysteine (Nazir and Naqvi 2010). The disproportionation of initially formed uranium(V) species into uranium(VI) and uranium(IV) may explain why only 37 % (relative to the initial uranium concentration) reduced uranium(IV) was found in the cells. The highest uranium(IV) level was detected 2 h after metal contact and decreased within 10 h. Calculations of the redox potential in the solution using the Nernst equation showed a shift towards more oxidizing conditions at lower uranium concentrations

(10 μM), but the opposite effect was detected at higher concentrations (50 μM). This clearly demonstrates that the redox behaviour plays a pivotal role in cellular uranium speciation and coordination.

Additionally, the environmental speciation should be taken into account; a basic overview was given by Choppin (2007). Different redox states of uranium were detected at the roots of a variety of *Arabidopsis halleri* (Viehweger and Geipel 2010). This plant was collected from a former uranium site in Johanngeorgenstadt (Germany). By sequential extraction of soil samples, a correlation was found between low bioavailability of the nutrient iron and the uptake of non-essential uranium. As reduction of Fe(III) to Fe(II) on the roots is a prerequisite for iron uptake, uranium reduction could take place in the same way. Laser-induced photoacoustic spectroscopy (LIPAS) confirmed a reduction of uranium(VI) to uranium(IV) which is proposed to occur by reduction of uranium(VI) to uranium(V) followed by disproportionation, generating uranium(IV) on the roots.

Arabidopsis plants grown under natural conditions, such as on rock piles, accumulate ~35 mg kg^{-1} uranium (dry weight) in the roots and ~17 mg kg^{-1} in the shoots (Viehweger and Geipel 2010). Taking into account only the bioavailable uranium in the soil, the soil to plant transfer factor was calculated to be 1.2 for roots and 0.6 for shoots. However, in hydroponically grown plants in the laboratory, uranium uptake was about 100-fold higher for roots and 10-fold higher in shoots when the concentrations are compared to natively grown plants. This dramatic increase in uranium uptake was attributed to iron deficiency in the hydroponic system. Fluorescence spectra of leaves and chlorophyll extracts indicated the occurrence of a flavonoid after uranium contact which could act as a possible chelator of the metal.

Another approach should be the comparison with the cellular behaviour of other heavy metals. A good clue is iron because a possible interaction between the uptake of the micronutrient iron and uranium was proposed (Viehweger and Geipel 2010). Additionally Caldwell et al. (2012) published a notable relationship between iron and uranium plant concentrations (correlation: 0.783; r-squared: 0.613). As some metals are micronutrients, their bioavailability has an impact on plant uranium uptake. A lot of knowledge concerning transition metal chelation and translocation inside plants and cells has been emerged during the last years. Reviews are found by Kraemer et al. (2007) or Kobayashi and Nishizawa (2012). Some of the discussed chelators such as citrate, nicotianamine or phenolics are able to chelate uranium too, whereas most of the transport mechanisms are shared by various metals which could include uranium. Figure 2 depicts the different discussed interactions between the actinide, soil and plant which all influence the metal speciation in a complex network.

An additional tool for the localization and characterization of processes involving metals has been highlighted (Donner et al. 2012). The authors suggest the use of synchrotron techniques for the determination of metals inside plant cells. XAS-based methods are element-specific as well as sensitive to the environment of the metal ion and are expected to play an important role in the study of the interactions of metal ions with living cells in the future.

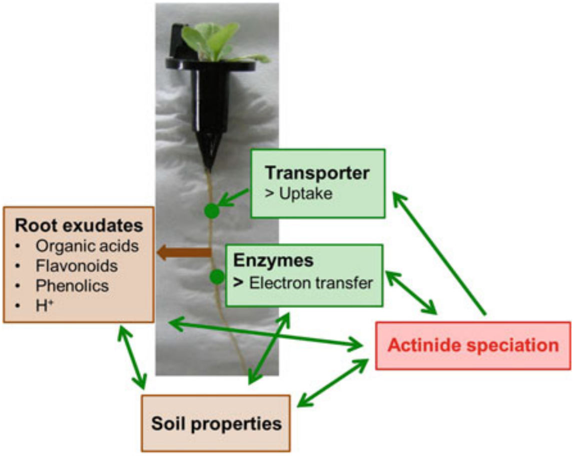

Fig. 2 Scheme of the complex network influencing the actinide speciation with focus on plant roots. *Green colour* refers to enzymatic ("biochemical") activity, whereas *brown colour* indicates chemical activity. Note that the activity of soil micro-organisms is neglected here

5 Neptunium

Neptunium is a radioelement generated in nuclear reactors as a by-product. The most stable isotope is ^{237}Np with a half-life of 2.14E06y. The oxidation states range from +3 to +7 with +5 as most stable oxidation state. Studies in plant sciences with neptunium are done mostly in the same way as for most of the other actinides, which means the determination of uptake.

Garden et al. (1986) studied the plant uptake of ^{237}Np into foliage of radish, chard and turnip depending on the soil pH. With increasing pH of the soil, the uptake of all plants decreases. This behaviour is clearly connected to the sorption properties of Np to the soil.

Also the behaviour of ^{237}Np in a marine environment towards water plants was studied (Germain and Pinte 1990). Highest ^{237}Np concentrations were determined to about 2.5 μg kg^{-1} wet weight in the red algae *Corallina officinalis*. These red algae have a bushy and well-calcified structure. The higher Np concentration compared to other biological species in this environment has been explained by the high affinity of Np towards carbonate surfaces.

6 Plutonium

Plutonium was discovered in 1940 be G.T. Seaborg and his group. The isotope with longest half-life is ^{244}Pu (8.1E07y). However, due to the production of nuclear energy and nuclear weapon, the fissionable isotope ^{239}Pu (half-life 24100y) is much more important in the environment.

Uptake of plutonium by plants has been much less studied than that of uranium, but critical overviews are available (Auer 1993; Coughtrey et al. 1984). This may be due to the problems connected with generating contaminated soil. Two pathways of assimilation are known: direct deposition from radioactive fallout on leaves or by roots. In contrast to other radionuclides, most of the plutonium distributed by radioactive fallout is found in the topsoil and may be re-suspended in the air as dust. The plutonium may be absorbed by the plant via leaves. The transfer factor via this way was estimated to be 0.02 (Bunzl and Kracke 1987, 1990). The transfer factor via roots should be several orders of magnitude lower; a value of 0.0005 has been proposed (Bunzl and Kracke 1990), consistent with previous estimates (Haunold et al. 1987). The overall estimates of transfer factors range from 1×10^{-7} to 2×10^{-4}. Uptake of plutonium via roots is limited by its solubility in the soil (Garland et al. 1981).

The order of soil–plant transfer of actinides is proposed to be the following: $\mathrm{Np} \gg \mathrm{Am} \sim \mathrm{Cm} > \mathrm{Pu}$ (Pimpl 1998). Supporting studies were performed inside a greenhouse over 7 vegetation periods. The soil was contaminated artificially with ^{237}Np, ^{238}Pu, ^{241}Am, and ^{244}Cm at levels of 1–20 Bq g^{-1} dry mass. The highest transfer factors were measured for grass and corn. The observed transfer of actinides from soil to the plants depended on the chemical properties of the particular ion but was also influenced by the properties of the soil.

Garland pointed out that plutonium is freely transported through the xylem of soya bean plants during their growing period (Garland et al. 1981). However, this indicates that the plutonium should be in a soluble chemical form. In the later stage of flowering, the plutonium seems to be fixed and not remobilized. It is also suggested from experiments providing the Pu as DTPA complex that the chemical form of plutonium changes during the absorption in the roots. In grown old leaves and roots, the Pu was associated with organic components having molecular weights >10,000. In the stems, the Pu is bond to fractions with molecular weights between <10,000 and >500. In the mature seeds, 85 % of the Pu was found in the hull and only 14 % in cotyledon.

A comparative study of interaction of organic components in the xylem exudates of soya bean with heavy metal ions was published in 1988 (Cataldo et al. 1988). It was found that Fe(III) and Pu(IV) are primarily bound to organic acids, while Ni(II) and Cd(II) are associated with the amino/peptide fraction. Nickel and iron containing complexes vary also with the age of the plant, and there are hints that these complexes are related to the concentration of the organic ligands produced and transported in the xylem. On the other hand for plutonium and cadmium, no relationships could be established to indicate the possible plant induction process.

Somewhat newer studies of the plutonium uptake from soils were performed by Lee et al. (2002a, b). In the first study, plants were grown in hydroponic media which was contaminated with plutonium at different concentrations and in different chemical forms. The ^{239}Pu concentration ranged from 8.0 to 16.0 μg L^{-1}. The used chemical forms were nitrate, citrate and DPTA. In case of nitrate and citrate, no correlation was found between the concentration in the tissues and the applied Pu concentration. However, the DTPA complex showed increasing transport to the shoots, whereas the concentration in the roots was lower. For Indian mustard (*Brassica juncea*), the found concentration in the shoots was up to ten times higher then for sunflowers (*Helianthus annus*). The uptake depended also on the DTPA concentration. Indian mustard had the highest uptake at 10 mg L^{-1} DPTA. In sunflower, the Pu uptake reached a maximum of 5 mg L^{-1} DPTA. In the second study (Taylor 1998), the hydroponic solution was exchanged by soil. For Pu contamination of the soil, the same components (nitrate, citrate, DTPA) were used, but the Pu concentration ranged from 19 to 100 μg kg^{-1}. A sequential extraction of the Pu in the soil was performed to determine the distribution of Pu in the various soil fractions. The lowest extractable Pu was found for Crockett soil with a pH 6.55. This soil contains large amount of clay which may adsorb the plutonium. The two other soils were Crawley soil and calcareous Weswood soil. However, also other constituents such as carbonate, salt concentration, metal oxide as well as the pH of the soil influence the extractable Pu. In the acidic Crawley soil, the only difference for nitrate and citrate medium was found for Indian mustard, and here, the uptake in the nitrate containing contaminant was significantly higher. The uptake increased with increasing DTPA concentration, but no relationship was observed. Highest uptake values were observed for the Crawley soil. No data for plant compartments were given in this publication.

7 Americium, Curium and Higher Actinides

Americium and Curium were discovered in 1994 by the group of G. T. Seaborg. The longest half-life americium isotope is ^{243}Am (7.34E03y), and the most stable Cm isotope is ^{247}Cm, with a half-life of 1.56E07 years.

These later elements in the series of actinides exist mainly in oxidation state +3 and so their biological effects are expected to be similar. Naturally occurring americium and curium have never been detected. They form trivalent ions in acidic solution. Both elements show fluorescence properties. Americium can be excited at about 508 nm, whereas Cm mostly is excited at 395 nm but the fluorescence lifetimes in aqueous media are very different: Am^{3+} about 17 ns and Cm^{3+} about 65 μs. Curium has an extraordinarily high fluorescence emission yield, which enables studies at extremely low concentrations, down to 10^{-11} M.

A TRLFS study estimated the stability of complexes of curium with ATP at trace concentrations of 3×10^{-7} M curium (Moll et al. 2005). Three species could be detected. Emission maxima at 598.6, 600.3 and 601 nm were assigned to $[Cm^{III}(H_2ATP)]^+$, $Cm^{III}HATP$ and $[Cm^{III}(ATP)]^-$, respectively, with fluorescence lifetimes of 88 μs, 96 and 187 ± 7 μs. The derived stability constants were $\log \beta_{121} = 16.86 \pm 0.09$, $\log \beta_{111} = 13.23 \pm 0.10$ and $\log \beta_{101} = 8.19 \pm 0.16$. The significantly higher lifetime for $[Cm^{III}(ATP)]^-$ was interpreted in terms of a possible ring structure that might be formed as the hydration number decreases, suggested by an increase of the fluorescence lifetime. Cm(III) forms the most stable ATP complexes while those of neptunium(V) are the weakest. Studies with the Nd(III)- and Sm(III)-transferrin complexes allowed the formation constants of Am(III) and Cm(III) to be estimated as $\log K_1 = 6.3 \pm 0.7$ and $\log K_1 = 6.5 \pm 0.8$, respectively

(Taylor 1998). The biokinetics of curium and americium were compared in a review in 2008 (Menetrier et al. 2008).

This lack of adequate modelling encouraged a study of the speciation of curium in biological systems in more detail (Heller et al. 2011, 2012). TRLFS and FT-IR spectroscopy (for europium) allowed resolution of the following citrate complexes: $Cm^{III}(HCit)$; $[Cm^{III}(H_2Cit)(HCit)]^{2-}$; $[Cm^{III}(HCit)_2]^{3-}$; and $[Cm^{III}(Cit)_2]^{5-}$. The respective stability constants were estimated to be $\log \beta_{111} = 21.0 \pm 0.2$, $\log \beta_{1(21)(11)} = 43.8 \pm 0.3$, and $\log \beta_{122} = 38.4 \pm 0.7$. An estimate of $\log \beta_{102}$ could not be determined. In addition, indications of the formation of $[Cm^{III}(Cit)]^-$ were seen. Structural parameters for both $Eu^{III}(HCit)$ and $[Eu^{III}(Cit)]^-$ were found by FT-IR spectroscopy and compared to DFT calculations. There is evidence for the binding of the metal to an hydroxylato group in $[Eu^{III}(Cit)]^-$. The authors concluded that in human urine with pH values <6, curium is present mainly as $[Cm^{III}(H_2Cit)(HCit)]^{2-}$ while europium is present as a mixture of $[Eu^{III}(H_2Cit)(HCit)]^{2-}$ and $EuHCit^0$.

However, up to now, only soils to plant transfer factors of these elements are determined. An early comparison is given by Schreckhise and Cline (1980). Lowest uptake was found for plutonium, whereas the data for americium and curium are comparable and about one order of magnitude higher. Highest values were determined for neptunium. This behaviour is clearly connected to the chemical properties of these elements in the soil. Due to effective charge (Runde 2000) of the actinide ions, which is connected to the oxidation state, the sorption decreases in the order $Pu > Am \sim Cm > Np$.

One of the very rare studies on the distribution of radionuclides in aquatic plants was performed by Zotina et al. (2008). They studied ^{241}Am concentration in elodea (*Elodea canadensis*) and in the water moss fontinalis (*Fontinalis antipyretica*). It was found that in both plant species, the americium distribution depends on chemical forms. It has been shown that about 5 % of the americium is in an intracellular soluble fraction and about 95 % is bond to the cell wall. The lowest Am content was found in lipids, whereas highest Am levels were linked to polysaccharides. Proteins and carbohydrates were found to bind about 10 % of the americium. It is surprising that the extraordinary fluorescence properties, especially of the element curium, did not result in more studies of the biological behaviour of these two elements. The higher actinides elements, starting with berkelium, have not yet been used for biological studies. This may be due to their low availability as well as due to the short half-lives of these isotopes. The most stable isotopes are ^{247}Bk with a half-life of 1400y and ^{251}Cf (700y).

8 Conclusion and Future Prospective

The behaviour of actinide elements in biological systems is mainly described by studies of transport and storage of these ions. Nevertheless, it can be expected that, in the future, identification of speciation in these processes becomes more important.

As plants need their surrounding contact medium to incorporate heavy metal ions such as actinides, it will be also of importance to study the interaction of metal ions with organic anions exuded from the roots. Besides well-known complexing agents, such as citric acid, also other ligands, for example, malate, succinate and fumarate may come into the fore (Ryan et al. 2001).

The very interesting possibility to visualizing metal ions within living cells has been reviewed (Dean et al. 2012). The use of fluorescent sensors in microscopy and spatially resolved mass spectrometric methods has the potential to detect the localization of metal ions within cells and their compartments. Up to now, this approach has been applied only to some important heavy metal ions. In addition, exploration of processes of incorporation of actinide ions into cells, their forms of storage and the excretion processes will all take centre stage in the future.

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Kinetic Models for Representing the Uptake of Radionuclides in Plants

M. C. Thorne

Abstract Traditionally, radionuclide accumulation in plants due to uptake from soil has been estimated using empirically measured concentration ratios. However, over the last 40 years, there has been an increasing interest in representing radionuclide transport in soils and uptake by plants using a kinetic approach. Here, a brief account is given of the processes involved and of the fundamental equations used to represent the kinetics of radionuclide transport and plant uptake. In this account, the focus is on developing an appropriate representation of soil hydrology to provide water fluxes for use in the advective–dispersive transport equation. Following this account, a description is given of various models that have been used to represent radionuclide transport in soil–plant systems. These models illustrate how a wide variety of factors such as sorption, active uptake by roots, plant growth, changing hydrological conditions and volatilisation have been taken into account. In addition, a summary is given of how plant uptake of ^{14}C can be estimated when the ^{14}C enters the soil zone from below as either carbon dioxide or methane.

Keywords Radionuclides · Soil–plant model · Kinetics · Soil hydrology · Bioturbation · Volatilisation · Carbon-14

Contents

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1 Introduction

Conventionally in radiological impact assessment studies, the uptake of radionuclides by plants from soil is represented using concentration ratios between plant tissues and the top layer of the soil down to a depth of 0.1 or 0.2 m. This is sometimes described as an equilibrium model, but it rather represents an empirical approach in which the measured concentration in the plant part at harvest (or at sampling for pasture, as this does not have a well-defined time of harvest) is compared with the measured concentration in soil. There is no implication that an equilibrium relationship between plant and soil concentrations exists at harvest or at the time of sampling, or even that such an equilibrium would ever be attained.

The concentration ratio approach has been extremely useful in radiological impact assessment studies relating to routine releases, but is less relevant to short-term intentional or accidental releases, when the time from deposition to harvest may be an important consideration. Furthermore, it does not provide a useful conceptual framework for investigating how transient aspects of the soil–plant system, e.g. the changing water content of the soil, influence plant uptake.

Because the uptake of contaminants by plant roots is closely related to soil properties such as water content and redox potential which also influence the migration of those radionuclides in soil, it is important to treat radionuclide transport in the soil and uptake by plants in an integrated fashion. It is also convenient to treat radionuclide transport in plants following root uptake within the same conceptual framework.

Following this introduction, Sect. 2 describes the processes that need to be taken into account when modelling radionuclide transport in soil and uptake by plants, Sect. 3 then describes an early approach to the kinetic modelling of agricultural soil–plant systems and how this was taken forward in a subsequent model. Section 4 then describes some more recent models of such systems. Modelling the uptake of ^{14}C from soils raises some special issues, and these are addressed in Sect. 5. Finally, Sect. 6 provides some conclusions and identifies potential directions in which this field might develop. To keep the discussion to a reasonable length, models for radionuclide transfers in forest ecosystems are not addressed in this chapter.

2 Processes to be Represented

For most radionuclides, transport in the soil column is by advection–dispersion in soil solution. Thus, a prerequisite for modelling radionuclide transport is an appropriate representation of the flow of soil water. Conventionally, this is addressed through the use of Richards' equation (Richards 1931). In one dimension vertically, this can be written in terms of two relationships.

$$\partial\theta/\partial t = -\partial q/\partial z \tag{1a}$$

$$q = -K(\theta)\partial\{\psi(\theta) + z\}/\partial z = -K(\theta)\{\partial\psi(\theta)/\partial z + 1\} \tag{1b}$$

where θ (−) is the fractional water content of the soil, t (s) is time, q (m s^{-1}) is the flow rate of water in the soil, z (m) is the vertical height in the soil column, $K(\theta)$ (m s^{-1}) is the unsaturated hydraulic conductivity of the soil and $\psi(\theta)$ (m) is the pressure head.

The form of Eq. (1a, 1b) has been used to emphasise that the advective water flow rate is implicit in Richards' equation. Note that the velocity of water flow is given by q/θ.

The hydraulic conductivity and the pressure head are both functions of the water content. Various parameterisations have been specified for the relationship between water content and the pressure head (or suction), e.g. those of Brooks and Corey (1964) and van Genuchten (1980), as discussed by Fredlund and Xing (1994) and Wheater et al. (2007). Specifically, the van Genuchten (1980) relationship is conventionally written (Wheater et al. 2007) as:

$$S_e = (\theta - \theta_r)/(\theta_s - \theta_r) = [1/(1 + |\alpha\psi(\theta)|^n)]^{-(1-1/n)} \quad \text{for} \quad \psi(\theta) < 0 \tag{2}$$

where S_e (−) is the degree of saturation, θ_s (−) is the saturated moisture content, θ_r (−) is the residual moisture content and represents the soil moisture that cannot be removed by capillary suction, and α and n are model parameters.

A generic method for obtaining unsaturated hydraulic conductivities from the degree of saturation was developed by Mualem (1976). When applied to the van Genuchten (1980) relationship, this gives (Wheater et al. 2007)

$$K(\theta) = K_s S_e^{\eta}\left[1-\left(1 - S_e^{1/\mathrm{m}}\right)^{\mathrm{m}}\right]^2 \tag{3}$$

where η is a tortuosity factor obtained through calibration against observations (Schaap and Leij 2000).

In practice, for a vegetated soil, Eq. (1a) needs to be modified to allow for water uptake by plant roots (Wheater et al. 2007). Thus,

$$\partial\theta/\partial t = -\partial q/\partial z - u_w \tag{4}$$

where u_w (s^{-1}) is the rate of water uptake by plant roots.

When simulating radionuclide transport, it is conventional to represent sorption to soil solids by an equilibrium distribution coefficient or Kd (m^3 kg^{-1}) value (IAEA 2010). This approach is convenient because it allows transport to be described using a single equation. However, in more comprehensive models, Kd values can be replaced by kinetic rate coefficients representing sorption and desorption, respectively. In such models, transport in soil solution is represented by one equation and transport on soil solids, e.g. by bioturbation, by a second. Using the equilibrium sorption approach, the transport equation can be written (Wheater et al. 2007):

$$\partial[\theta C + S]/\partial t = -\partial\left[J_d + J_q\right]/\partial z - u_s - \Gamma \tag{5}$$

where C (Bq m^{-3}) is the concentration in soil solution, S (Bq kg^{-1}) is the concentration in soil solids, J_d (Bq m^{-2} s^{-1}) is the dispersive flux, J_q (Bq m^{-2} s^{-1}) is the advective flux, u_s (Bq m^{-3} s^{-1}) is the rate of uptake by plant roots and Γ (Bq m^{-3} s^{-1}) is the rate of radioactive growth or decay. Using equilibrium sorption,

$$S = \rho_b KdC \tag{6}$$

where ρ_b (kg m^{-3}) is the dry bulk density of the soil.

The dispersive and advective fluxes are given by

$$J_d = -\theta D_h \partial C/\partial z \quad \text{and} \quad J_q = qC \tag{7}$$

where D_h (m^2 s^{-1}) is the sum of the soil molecular diffusion coefficient, taking into account the tortuous nature of the solute pathways, and the mechanical dispersion coefficient, which is often written as $d_L q/\theta$, where d_L (m) is the soil dispersivity.

Wheater et al. (2007) used the work of Epstein (1966), Nye and Tinker (1977) and Barber (1984) to argue that the active uptake of various chemicals (including radionuclides) across the root boundary can be represented by Michaelis–Menten kinetics, i.e.

$$F = F_{\max} C_b/(k_m + C_b) \tag{8}$$

where the concentration at the root boundary C_b (mol m^{-3}) can be equated to the concentration in bulk soil solution, F (mol s^{-1} m^{-2}) is the flux per unit area of root boundary and $F_{\max}$ (mol s^{-1} m^{-2}) and k_m (mol m^{-3}) are coefficients specific to the chemical under consideration.

In practice, radionuclides are normally present in trace quantities in soils, so Eq. (8) can be linearised to give

$$F_r = \alpha C \tag{9}$$

where F_r (Bq s^{-1} m^{-2}) is the radionuclide uptake rate per unit area of root, α (m s^{-1}) is the root absorbing power (Nye 1966) and C (Bq m^{-3}) is the radionuclide concentration in soil solution, as defined previously.

From this, it follows that

$$u_s = 2\pi a \rho_r \alpha C \tag{10}$$

where a (m) is the mean root radius and ρ_r (m m^{-3}) is the total root length per unit volume of soil.

The approach outlined above has some limitations. Specifically, it treats sorption as being a reversible process. This ignores the possibilities that radionuclides can be incorporated irreversibly within soil solids, may be precipitated or co-precipitated from soil solution and may be incorporated in organic matter in soils from which they may be released only through mineralisation of the organic matter. Also, it ignores the possibility that some radionuclides, such as isotopes of selenium, may be volatilised from soils and plants (Sheppard and Sheppard 2008; see also Pérez-Sánchez et al. 2012).

Bioturbation also has to be considered in modelling the transport of radionuclides in soils. In agricultural soils, mass transport of soil solids is primarily mediated by earthworms. Shallow-burrowing earthworms are predominantly active in the top 10–25 cm and consume earth, primarily burrowing in a horizontal direction. Deep-burrowing earthworms mainly occur in the top 45 cm and primarily burrow in a vertical direction, coming to the surface to ingest foliage and other organic matter. The deepest burrowing earthworm is *Lumbricus terrestris*, which is mainly found within the top 1 m, but has been observed at depths of up to 2.5 m (Bishop 1989).

Bishop (1989) noted that the amount of earthworm activity is dependent on the type of soil, the type of land use and the time of year. The habitats likely to support the greatest densities of earthworm population are base-rich pastures and orchards where the soil is fairly well drained and loamy in texture. The lowest densities are associated with acid moorlands where the soils are shallow and peaty. Earthworm activity is found to be high in both the spring and the autumn and low during the summer and winter.

For a one-dimensional vertical soil model, the bioturbation rate needs to be based on the amount of soil redistributed vertically rather than the total amount of soil ingested and egested by earthworms. This can be estimated from the total amount of earthworm casts deposited on the surface. Bishop (1989) reports a range of 0.25–6.18 kg m^{-2} y^{-1} for a variety of arable and pasture farmland. Müller-Lehmans and van Dorp (1996) reported a range of 1.88–13.40 kg m^{-2} y^{-1} for European pasture and recommended a value of 6 kg m^{-2} y^{-1}, with 2 kg m^{-2} y^{-1} coming from deeper soil (greater than 25 cm in depth).

Recently, Klos et al. (2014) have introduced bioturbation into a radionuclide transport model in which the soil column is divided into 0.2-m-thick layers. In this model, the rate coefficients between the soil layers were augmented by adding a term $M_{\mathrm{i,j}}/\rho_{\mathrm{i}}d_{\mathrm{i}}$, where $M_{\mathrm{i,j}}$ (kg m^{-2} y^{-1}) is the rate at which soil is moved from layer i to layer j by bioturbation (expressed on a dry weight basis), ρ_{i} (kg m^{-3}) is the dry bulk density of soil in layer i and d_{i} (m) is the depth of layer i. In general, mass balance considerations dictate that $M_{\mathrm{i,j}} = M_{\mathrm{j,i}}$ for any i and j. The values of $M_{\mathrm{i,j}}$ used by Klos et al. (2014) are listed in Table 1.

3 An Early Approach to Kinetic Modelling and Subsequent Developments to that Approach

Prior to the early 1980s, soil–plant models tended to be very simple. The soil was typically treated as a single well-mixed layer, and plant uptake was estimated by applying a plant/soil concentration ratio to the radionuclide concentration

Table 1 Bioturbation rates used by Klos et al. (2014). Soil layer thicknesses are 0.2 m

Parameter	Value (kg m^{-2} y^{-1})	Parameter	Value (kg m^{-2} y^{-1})
$M_{1,2}$	0.54	$M_{2,1}$	0.54
$M_{2,3}$	0.42	$M_{3,2}$	0.42
$M_{3,4}$	0.30	$M_{4,3}$	0.30
$M_{4,5}$	0.18	$M_{5,4}$	0.18
$M_{5,6}$	0.06	$M_{6,5}$	0.06

estimated for that layer. External contamination of plants was represented by applying a single exponential loss function to the initially deposited activity, and little consideration was given to translocation of external deposits to internal plant tissues (Coughtrey and Thorne 1983). However, in 1983, Coughtrey and Thorne (1983) described new dynamic mathematical models for simulating radionuclide transport in soils, plants and domestic animals. These models (the SPADE system) took account of the need to be able to simulate a wide variety of different agricultural practices over a wide range of timescales. The soil–plant model concentrated on the topsoil. Thus, in the model, the soil was distinguished into ten layers each 0.03 m thick. In each layer, three components were identified: soil solution, organic matter and inorganic matter. Downward transfers were postulated for each of these components; that is, the model was developed only for initial deposition at the surface, and the mechanisms of transfer were not specified. Within each layer, exchange processes were postulated between soil solution and both organic and inorganic matter. Thus, soil solution acted as the medium of exchange between these other components.

In the SPADE system, plants were modelled as being composed of up to six well-mixed compartments. These comprised root, 'root store', stem, internal leaf, external leaf and grain or fruit. The 'root store' compartment was introduced so that the model could represent root and tuber crops, as well as allowing distinctions to be made between annual, biennial and perennial species. Leaves were distinguished into external and internal components to allow particulate deposition to be distinguished from incorporation.

In order to limit the number of rate coefficients that had to be specified separately, some simple rules were introduced governing the rate of transport in soil solution (constant with depth), the rates of exchange between soil solution and both organic and inorganic matter (exponential variation with depth), the rates of vertical transport of both organic and inorganic matter (exponential variation with depth) and the rate of root uptake (multi-exponential variation with depth).

The SPADE modelling system was used by the UK Ministry of Agriculture, Fisheries and Food (MAFF) and latterly by the Food Standards Agency (FSA) through to about 2005. Subsequently, it has been replaced by the PRISM model. This was initially described in a set of conference papers (Maul et al. 2005; Thorne et al. 2005; Robinson et al. 2005), and the most recent version is detailed in full in a set of technical reports (Walke et al. 2012a, b; Watson 2012).

The soil–plant model adopted in PRISM is substantially different from that in SPADE and is described in some detail below.

To represent the soil, ten soil layers are again used, so that the model has a well-defined compartmental structure. Typically, the superficial litter layer will be thin (~ 0.01 m), and this is layer 1. For farmed soils, the A horizon is typically about 0.3 m thick. To maintain sensible vertical discrimination, this is split into 3 layers of thickness 0.1 m (layers 2–4). The B horizon plus substrate goes down to about 2 m to conform to the HOST hydrological scheme that is applicable to the whole of Britain (Institute of Hydrology 1995). However, cereal roots are likely to penetrate to depths of up to 1 m and deep ploughing could go to a depth of more than 0.31 m, so it is necessary maintain more discrimination in the top of the zone. Layers 5–8 have a thickness of 0.2 m and layers 9 and 10 thicknesses of 0.45 m. This gives an overall soil profile depth of 2.01 m.

For the purpose of assigning properties, each layer is considered to be of one of three textures: sand, clay or loam.

Plants are distinguished into seven components, as shown in Fig. 1. Transfer rates between the different plant components are specified directly in the model based on empirical observations, but, in broad terms, a distinction is made between elements that are actively transported in the phloem and those that are not (Walke et al. 2012b).

The water content of each of the vertical compartments in the soil is computed by mass balance, taking account of precipitation input (P), evapotranspirative losses (E_i), flows between layers ($I_{\mathrm{i},\mathrm{i}+1}$ and $I_{\mathrm{i}+1,\mathrm{i}}$, with the special case to groundwater (G) at the base of the model) and sub-horizontal drainage (H_i).

A feature of the PRISM model is that plant growth is explicitly represented. The plant types included in the model are mixed pasture, leguminous pasture, non-leguminous fodder crops, leguminous fodder crops, cereals (including winter-sown and spring-sown options), non-leguminous green vegetables, leguminous green vegetables, root vegetables, tubers, tree fruit, shrub fruit and herbaceous fruit. Growth functions are defined for individual plant components (foliage, stem, fruit/grain and roots) and require the final aboveground biomass (W), the time when growth starts for each component (t_start), the time when growth ceases for each component (t_end) and a growth power (N).

The general form of the growth model for any plant component is

$$w(t) = 0 \quad t \le t_\mathrm{start} \tag{11a}$$

$$= W[(t - t_\mathrm{start})/(t_\mathrm{end} - t_\mathrm{start})]^N \quad t_\mathrm{start} \le t < t_\mathrm{end} \tag{11b}$$

$$= W \quad t \ge t_\mathrm{end} \tag{11c}$$

where $w(t)$ is the mass of the component at time t.

The value of N is typically 2.2.

The PRISM root profiles are determined based on root-shape modifiers, which are defined as the ratio of root density in a particular soil layer in field conditions to

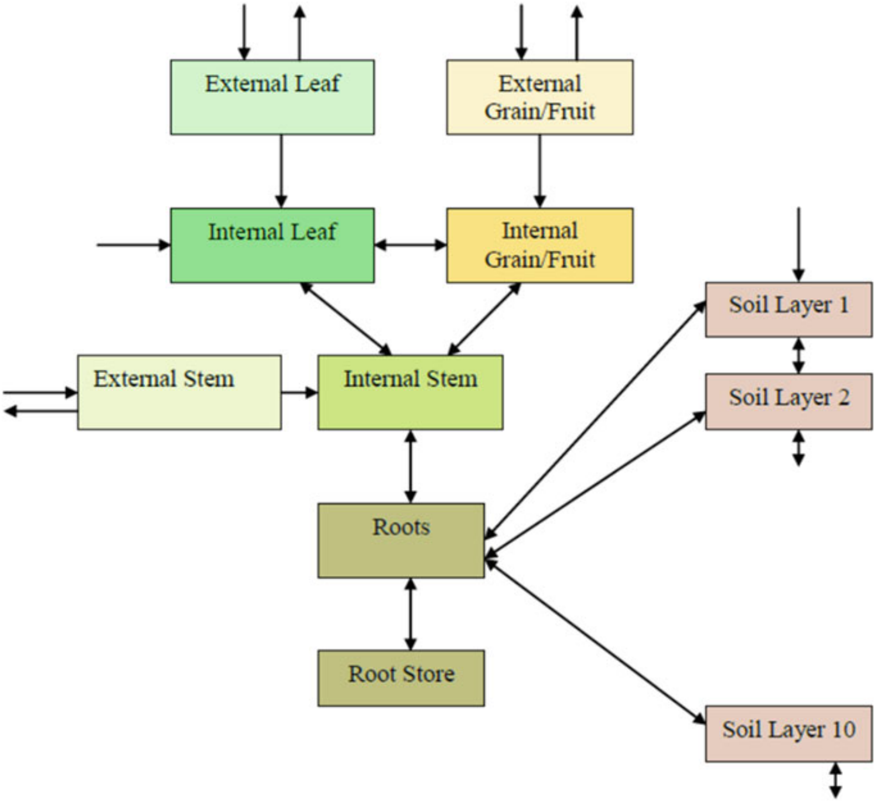

Fig. 1 Structure of the PRISM soil–plant model. (From Walke et al. 2012b)

that in pot experiments, *s*. Root growth is also dependent on a root profile development power, *v*. For a mature crop, reference values of *s* of 1 are used for soil layers 1–3, as a well-developed root system in the field should approximate closely to a well-developed root system in a pot, providing that the pot is not highly restrictive of the root system. Values of *s* for the deeper layers are defined by reference to observed root profiles. These are primarily taken from Bishop and Beetham (1989). The equation representing root growth in a soil layer is

$$s(t) = S[w_\mathrm{r}(t)/W_\mathrm{r}]^v \tag{12}$$

where $w_\mathrm{r}(t)$ is calculated as in Eqs. (11a, 11b, 11c) and S is the value of s that applies when the plant is mature. The development of $s(t)$ for winter-grown cereals is illustrated in Fig. 2.

Alternatively, an exponential root-shape model may be used. Such a model was developed by Gerwitz and Page (1974) and was applied by Wheater et al. (2007) to

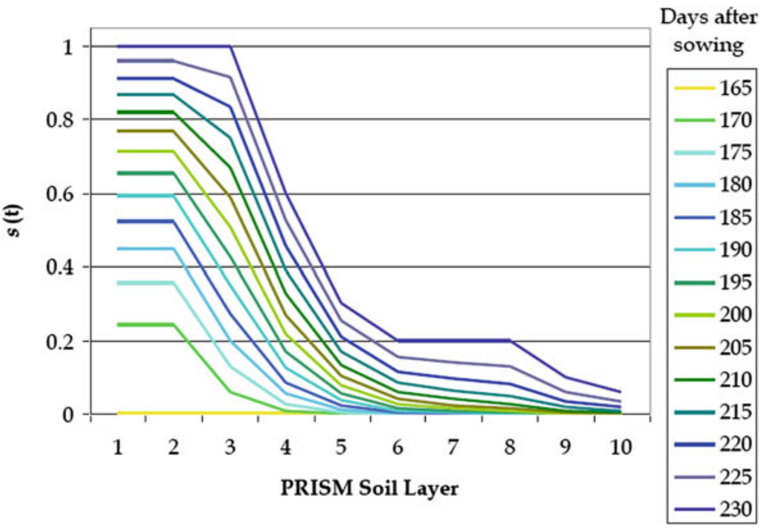

Fig. 2 Development of root-shape modifiers for winter cereals. (From Walke et al. 2012b)

a series of root density measurements of wheat taken by Burne et al. (1994). This model has the form

$$\rho_r(z,t) = \rho_{r0}(t)\exp[z/z_r(t)] \tag{13}$$

where $\rho_{r0}(t)$ is the root density at the soil surface at time t, z is the depth from the surface and $z_r(t)$ is the time-dependent root attenuation coefficient.

An important innovation in the PRISM model was that it used the degree of sorption of radionuclides to soil solids to adjust empirically observed plant–soil concentration ratios to make them of wider applicability. The argument is based on the consideration that with equilibrium, reversible sorption, a contaminant is partitioned between soil solution and soil solids. The uptake affinity, δ, is defined relative to soil solution containing unit concentration of the radionuclide. Thus, the plant/soil concentration ratio, *CR*, as conventionally defined is given by'

$$CR = \delta/(\theta + \rho_b Kd) \tag{14}$$

hence, Eq. (14) can be inverted to give

$$\delta = CR(\theta + \rho_b Kd) \tag{15}$$

Values of δ are found to be much more consistent for individual radionuclides than are *CR* values. Furthermore, they allow the effects of time-dependent changes in soil moisture content, θ, to be explicitly taken into account.

4 More Recent Modelling Approaches

Based on some of the developments included in the PRISM model and other considerations specific to the behaviour of selenium in soils, Pérez-Sánchez et al. (2012) developed a kinetic model to represent the transport of ^{79}Se in soils and its uptake by plants.

As discussed by Pérez-Sánchez et al. (2012), within soils, selenium can be thought of as most resembling sulphur in its chemical behaviour (Wheater et al. 2007). Selenium exists as anionic complexes in groundwater and in four oxidation states: selenate(+6), selenite(+4), elemental Se(0) and selenide(–2) (Fio et al. 1991). The speciation of selenium is dependent upon a number of factors, such as pH, the soil redox potential (Eh), the mineralogical and chemical composition of the soil, microbial interactions and the nature of adsorbing surfaces (Neal 1995). However, redox potential exerts the most influence over selenium behaviour in soil (Moore 2004). Thus, in very oxidising conditions, selenate ($SeO_4{}^{2-}$) will tend to dominate selenium speciation (Fio et al. 1991; Neal 1995). As the redox potential falls under more saturated, reducing conditions, selenate will be successively reduced to selenite ($SeO_3{}^{2-}$), elemental selenium and selenide. This has important implications for the bioavailability of selenium (Moore 2004); the more reducing the soil conditions, the less soluble and mobile selenium becomes (Neal 1995).

Additionally, there is extensive evidence that selenium is volatilised from both soils and plants (Pérez-Sánchez et al. 2012; Sheppard and Sheppard 2008). Furthermore, selenium incorporated in plants can be transferred to the organic matter ‘pool’ in soil whence it will be returned to soil solution by mineralisation processes.

Based on the above considerations, Pérez-Sánchez et al. (2012) included in their model changes in soil hydrology and their effects on redox conditions, volatilisation from soils and plants, and the incorporation of selenium in organic matter in soil and its subsequent release. Of particular interest is the simplified approach to representing soil hydrology that they developed.

In the adopted approach, a 1D soil column is used. This soil column is considered either to drain from its base or to receive an upward groundwater flux from below. The former is appropriate to well-drained agricultural soils, whereas the latter is appropriate to discharge zones (e.g. riparian areas). These two situations are illustrated in Fig. 3.

The fundamental equation used to represent the situation shown in Fig. 3a is

$$\mathrm{d}h/\mathrm{d}t = \left[R_\mathrm{i} - ah^b - f_\mathrm{i}PE_\mathrm{i}\right]/\Delta\theta \tag{16}$$

where h (m) is the height of the water table at time t; R_i (m y^{-1}) is the average precipitation/irrigation rate in month i; PE_i (m y^{-1}) is the potential evapotranspiration rate for month i; a and b are calibration constants; f_i is the fraction of the potential evapotranspiration (PE) that constitutes actual evapotranspiration (AE); and $\Delta\theta$ is the difference in water content between soil that is fully saturated and soil that contains only some minimal water content.

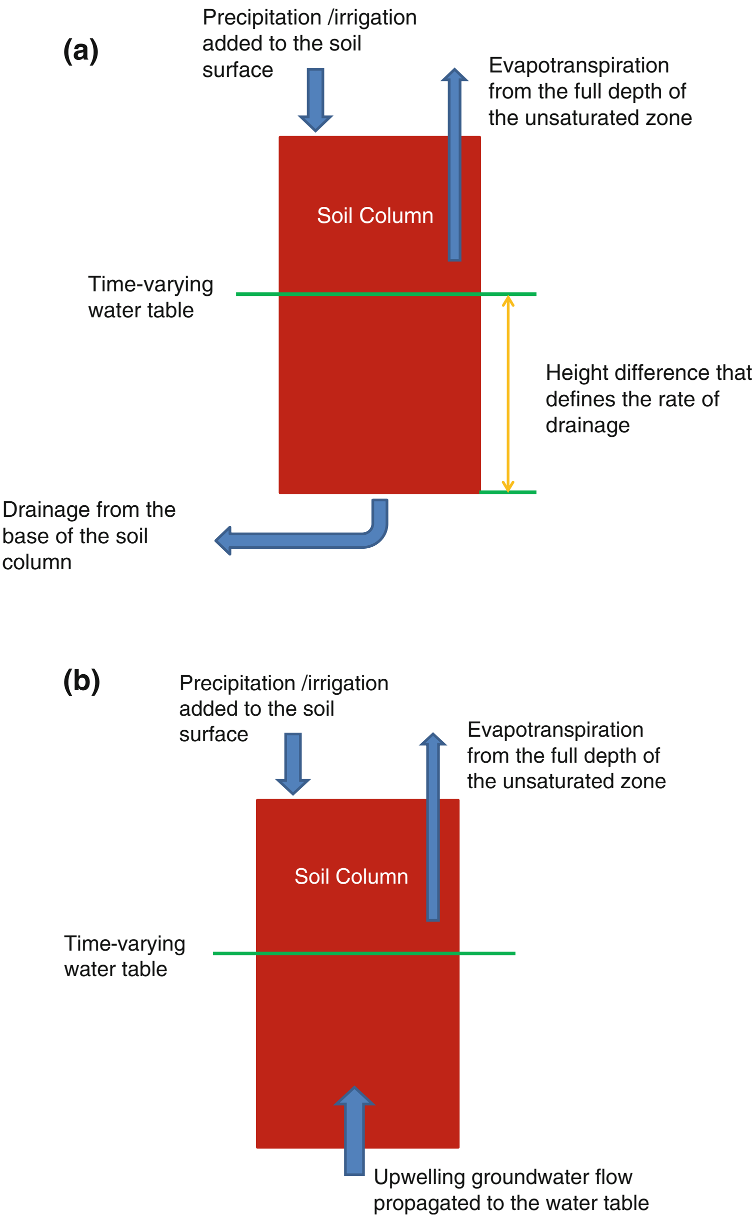

Fig. 3 Conceptual models for the hydrology of a freely draining soil column (**a**) and a column underlain by upwelling groundwater (**b**)

In the following, the month index i is generally suppressed for conciseness, but should be understood to apply throughout.

Additionally, a variable h_2 is defined and θ is allowed to vary from its value at the height of the water table (θ_1) to its value at height h_2 (θ_2). Linear interpolation is used over this range. Thus,

$$\theta = \theta_2 \quad z \geq h_2 \tag{17a}$$

$$\theta = \theta_1 + (z - h)(\theta_2 - \theta_1)/(h_2 - h) \quad h < z < h_2 \tag{17b}$$

$$\theta = \theta_1 \quad z \leq h \tag{17c}$$

It is readily shown that to increase the height of the water table by unit amount in unit area, it is necessary to add a volume of water $\theta_1 - \theta_2$, corresponding to $\Delta\theta$. Thus,

$$\mathrm{d}h/\mathrm{d}t = \left[R - ah^b - fPE\right]/(\theta_1 - \theta_2) \tag{18}$$

Losses through drainage are represented through the term $-ah^b$ with the rate of loss being a monotonically increasing function of the height difference between the water table and the base of the soil column.

However, where groundwater upwelling dominates, Eq. (18) is replaced by

$$\mathrm{d}h/\mathrm{d}t = [R + F - fPE]/\Delta\theta \tag{19}$$

where F is the upwelling flux of groundwater (m y^{-1}).

This approach neglects any losses by interflow downslope within the soil. This is cautious, since it maximises the upward transport of contaminants. However, if the water table reaches the surface, any excess water is taken to be expelled from the soil column and lost as overland flow. This excess water comprises both upwelling groundwater and precipitation that has never penetrated the soil column.

In the model, changes in the height of the water table are calculated on a monthly basis, with R and PE also specified on a monthly basis and F (as required) specified as a long-term constant value. Thus, in the groundwater-upwelling variant,

$$\Delta h = \Delta t[R + F - fPE]/\Delta\theta \tag{20}$$

In order to account for surface runoff when $h = H$ (i.e. the soil is saturated to the surface at height H),

$$h_\mathrm{n} = \min(h_\mathrm{o} + \Delta h, H) \tag{21}$$

where h_n is the new value of h and h_o is the old value of h.

The rate of surface runoff, S, is given by

$$S = \max(0, \{h_o + \Delta h - H\}\Delta\theta) \tag{22}$$

Having defined the location of the water table using the above approach, water fluxes between the various soil layers are computed differently for the zone beneath the water table and the zone above the water table. Above the water table, the water flux at height z, $F(z)$, is computed in the same way for both the draining and recharging cases, i.e.

$$F(z) = R - fPE + fPE(z - h)/(H - h) \quad H \geq z \geq h \tag{23}$$

However, below the water table, there may be a time-dependent drainage flux, D, or a constant upwelling flux, F. Thus, for cases 3a and 3b, the following alternative expressions apply:

$$F(z) = D = ah^b \quad h > z \geq 0 \tag{24a}$$

$$F(z) = -F \quad h > z \geq 0 \tag{24b}$$

Note that the convention used is that positive fluxes are directed downwards.

As water contents and water fluxes are defined in and between all the layers of the soil column, radionuclide transport can be represented using the advective–dispersive transport approach outlined in Sect. 2. In practice, in the model, the dispersive component is neglected and a purely advective approach is adopted. Sorption is taken into account using an equilibrium approach; that is, the effective volume of each compartment includes the effects of sorption. The model is normalised to a reference soil area, A, of 1 m^2. Thus, the effective volume of each soil layer i, V_i (m^3), is given by

$$V_i = Ad_i(\theta_i + \rho Kd_i) \tag{25}$$

where d_i (m) is the user-specified depth of the soil layer; θ_i (−) is the average water content of that soil layer obtained from the hydrological model; ρ (kg m^{-3}) is the dry bulk density of the soil; and Kd_i (m^3 kg^{-1}) is the distribution coefficient for that soil layer.

Above the capillary fringe, oxic conditions prevail and one value of the distribution coefficient (Kd_2) applies. Below the water table, anoxic conditions prevail and a second distribution coefficient (Kd_1) prevails. Between, a linear interpolation is assumed, i.e. at height z, where $h_2 > z > h$:

$$Kd(z) = Kd_2 + (Kd_1 - Kd_2)(h_2 - z)/(h_2 - h) \tag{26}$$

From the above, it follows that

$$\lambda_{\mathrm{ij}} = AF_{\mathrm{ij}} \big/ V_{\mathrm{i}} \tag{27}$$

where λ_{ij} (y^{-1}) is the rate coefficient for transfer from layer i to layer j (defining layer 0 as a sink for surface discharge and layer 11 as a sink for drainage through the base of the soil column).

By substitution from Eq. (25),

$$\lambda_{\mathrm{ij}} = F_{\mathrm{ij}} \big/ d_{\mathrm{i}}(\theta_{\mathrm{i}} + \rho Kd_{\mathrm{i}}) \tag{28}$$

Volatilisation from the soil is taken into account using a simple parameterisation, in which the volatilisation rate is dependent only upon the soil moisture content. It is argued that there are two considerations that will determine the evolution of volatile selenium from soil. These are the location of production and the ease of escape to the soil surface. Both of these will be related to the water content of the soil. The production of volatile forms is likely to be microbially mediated. As the most likely gases to be produced are methylated forms, production is likely to be concentrated at or below the water table, since methylation is unlikely to be significant in aerobic conditions (though minor anaerobic pockets may occur within the generally aerobic soil zone and volatilisation has been reported from aerobic soils). However, at depths significantly below the water table, selenium is likely to become dissolved and may be reutilised rather than released. In view of these considerations, a generalised loss rate model is specified in which the loss rate takes a constant (low) value for highly unsaturated soils, increases to a maximum for soils close to saturation and then remains constant or decreases to a constant value below the water table.

The available evidence suggests that volatilisation of selenium from plants occurs as a consequence of root uptake of selenium in solution and the subsequent production of volatile compounds within the plant (Limer and Thorne 2010). Therefore, the primary consideration is to develop a root uptake model for selenium in solution, since volatilisation can be represented as a loss process from the plant in competition with other loss processes such as cropping. The root uptake model developed by Pérez-Sánchez et al. (2012) is similar to that described above for PRISM and is not described further herein.

Cropping of plants is represented by a rate coefficient determined by the ratio of the rate of biomass removal and the standing biomass at any time.

In principle, a complex model for organic degradation and mineralisation reactions could have been included. However, Pérez-Sánchez et al. (2012) argued that because of uncertainties in how selenium mineralisation is related to carbon mineralisation, a complex approach is not justified, so a single rate constant for such degradation was defined. As the organic matter is likely to be present mainly in the upper layer of the soil system, this activity is returned to the uppermost soil layer.

Subsequently, Pérez-Sánchez and Thorne (2014) have adapted the selenium model described above to make it applicable to radionuclides in the ^{238}U decay chain. This enhancement now also includes a representation of bioturbation (Pérez-Sánchez and Thorne, Journal of Radiological Protection, in press) following that adopted by Klos et al. (2014).

The above discussion has emphasised vertical 1D models of radionuclide transport in soils and uptake by plants. However, 2D and 3D representations are also used. In particular, 3D, physically based, surface-water catchment models can be used to represent contaminant transport both in solution and as a consequence of sediment transport (Towler et al. 2011). Such models have been extensively used in the development of safety cases for the geological disposal of radioactive wastes (Bosson et al. 2010, 2012a, b). These models are not described here, as the principles for representing contaminant transport in the soil zone and uptake by plants are the same as applied in 1D.

5 Transport of Carbon-14 in Soils and Uptake by Plants

When ^{14}C is released to atmosphere, uptake by plants is relatively readily modelled. In general terms, the specific activity of carbon dioxide in the atmosphere at ground level is calculated and carbon with this specific activity is then used as the source material for photosynthesis and biomass production. As most plant carbon originates from foliar uptake from the atmosphere and subsequent photosynthesis, this approach is a good approximation to what physically occurs. TOCATTA (Le Dizès 2005; Le Dizès et al. 2012; Aulagnier et al. 2012, 2013) is a good example of a state-of-the-art model based on these principles.

However, when ^{14}C is released into the soil from below, e.g. from a near-surface facility for the disposal of radioactive wastes, different considerations apply. The ^{14}C is transported through the soil atmosphere by both diffusion and advection, the latter being controlled by variations in atmospheric pressure. In addition, the ^{14}C dissolves in soil solution and becomes available for root uptake. Although root uptake is generally a minor source of carbon for plants, typically contributing 1–2 % of plant carbon (BIOPROTA 2014), it can be a major source of ^{14}C, if the soil atmosphere is much enriched in ^{14}C relative to the aboveground atmosphere.

However, most of the ^{14}C that enters the soil system from below is released into the atmosphere above the soil. There, it may be temporarily retained in the plant canopy and be available for uptake by photosynthesis. As with uptake from soil, the significance of the sub-canopy uptake of ^{14}C can be enhanced by the higher specific activity of ^{14}C in the sub-canopy atmosphere than the above-canopy atmosphere.

Over the last few years, several models for transport of ^{14}C through soils and uptake by plants have been developed and compared (Mobbs et al. 2013). The most comprehensive model that has been developed is that produced for use in the post-closure radiological safety assessment of the UK Low Level Waste Repository (LLWR) (see Limer et al. 2011). More recently, new field studies have been reported on the transport of ^{14}C-labelled methane through soils in field conditions, its conversion to ^{14}C-labelled carbon dioxide and its uptake by plants. This work is underpinning the ongoing development of detailed, process-based and simplified, assessment-level modelling of the processes involved (Appendix B to BIOPROTA 2014).

6 Conclusions

Over the last 40 years, kinetic models for radionuclide transport in soils and uptake by plants have developed considerably. Nevertheless, for many assessment studies, reliance is still placed upon the use of empirically determined distribution coefficients and plant–soil concentration ratios. Compilations of recommended values and distributions for these factors continue to be produced (IAEA 2010), and experimental studies typically continue to be directed to their determination. It is recognised that experimental work to underpin comprehensive, process-based models is much more complex and resource intensive than the measurement of distribution coefficients and concentration ratios (Wheater et al. 2007). However, it repays the investment in terms of greater explanatory power, applicability in a wider range of circumstances and by identifying issues, such as the effects of time-dependent hydrology, that cannot even be fully articulated in a simpler modelling framework.

The earliest kinetic models, like SPADE, required the developer and/or user to estimate rate coefficients and then input them into the model. More recent developments compute the rate coefficients, which may be time dependent, from various sources of information. This information includes the empirical estimates of distribution coefficients and plant–soil concentration ratios that were used in earlier models. However, it also includes other information that could not previously readily be used, e.g. root uptake rates from studies in nutrient solution or kinetic studies of contaminant uptake on solids from solution.

The new models emphasise the importance of modelling changes in soil hydrology and soil chemistry. Currently, the models represent soil chemistry in a highly simplified way, using soil moisture content as a surrogate for redox conditions. It is anticipated that the next generation of models will include explicit coupling of hydrological, hydrogeological and hydrogeochemical processes in the soil zone, so that a much wider range of biogeochemical processes can be represented. Such an approach, in which 3D hydrological modelling is coupled to geochemical modelling, is already being explored in the sub-surface (Piqué et al. 2013), but its extension to the soil zone will require more detailed consideration of biological processes in a highly dynamic environment than is necessary at greater depths and will require that physiologically based models of plants are adopted, as in the COUP model (Jansson and Karlberg 2001). Also, models used at the present time typically represent a 1D soil column. Within this framework, simplifications and ad hoc approximations have to be made to ensure that a coherent hydrological situation is represented. It is anticipated that, in future, radionuclide transport in soils and uptake by plants will be more often simulated in 2D (hillslope) or 3D (surface-water catchment) contexts, by including appropriate soil–plant modules within the sorts of hydrological and hydrogeological catchment-scale models that already exist (Towler et al. 2011).

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Metal–Microbe Interaction and Bioremediation

S. R. Joshi, Debajit Kalita, Rakshak Kumar, Macmillan Nongkhlaw and Pynskhem Bok Swer

Abstract Bioremediation of heavy metals and radionuclides has shown immense promise as an alternative approach for cleaning up, especially the biosphere component of the environment. The ubiquitous nature of microbes has made them the pioneers in any bioremediation approaches. Understanding the working mechanism of these microorganisms either independently, or as a community in relation to their interaction with heavy metal will enlighten and improve the use of bioremediation for environmental cleanup. The discovery of plants that have metal accumulation potential has opened fresh avenues for bioremediation. Plant-based bioremediation is still at a nascent stage, but it has attracted considerable attention in recent years. A concerted approach of using plants and microbes for bioremediation is another strategy that might work efficiently as both can complement each other through various interactions. Moreover, genetic engineering can be used to improve the bioremediation capacity of both plants and microbes and further improve their capacity in bioremediation of heavy metals and radionuclide.

Keywords Bioremediation · Microbes · Heavy metals · Radionuclides

Contents

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1 Introduction

The continuous growth of human population has resulted in the increasing demand for basic life-supporting commodities worldwide. There has also been a concomitant increase in the industrialization process to meet the basic human demands. Furthermore, this has led to the increase in energy demands that are partly met by nuclear energy. Nuclear energy is an important alternative energy source which accounts for 17 % of the overall electricity of the world. As a consequence, mining for radioactive elements like uranium is crucial, which has led to the large amounts of toxic chemicals being released into the environment either deliberately or accidentally. These toxic contaminants include radionuclides like uranium and heavy metals such as lead, cadmium arsenic, and mercury. Heavy metals like copper, zinc, cobalt, and iron are essential micronutrients for both plants and microorganisms, but if present at higher concentration, they can impair various metabolic processes. Other metals like lead, cadmium, mercury, and uranium have no known biological functions and are toxic even at lower concentrations. Inorganic contaminants like heavy metals and radionuclide are not degradable and tend to accumulate in the environment for a long time (Sarma et al. 2004; Renshaw et al. 2005). Several technologies have been developed to address the problem of heavy metal and radionuclide contamination as they pose serious ecological and health hazards. To compensate the higher cost involved in the newer technologies, alternative methods have been explored to address this issue.

Natural habitats harbor abundant and diverse type of microorganisms which can be explored for bioremediation processes. However, there is a need for the identification and characterization of the microbial strains that reveal high metal accumulation capacity and specificity. Uranium-tolerant bacteria have been isolated from various uranium-mining sites and deposits (Kumar et al. 2011, 2013a; Sarma et al. 2012, 2013). Bacteria from uranium deposits have been characterized for their metal tolerance and uranium binding (Kumar et al. 2011, 2013a; Sarma et al. 2012, 2013). Understanding and exploring the microbe–metal interaction have resulted in an upsurge in the research interest with their importance in various high-throughput biotechnological applications such as biosensor, biofuel cells, and most promisingly in microbe-mediated nanomaterial synthesis (Devi and Joshi 2012). Identification of the microbial ligands/cellular processes involved in metal sequestration has lead to the development of engineered organisms with various cell surface displays that facilitate their applications in industrial catalysis, biosorption, bioremediation, biofuel, and biosensor technology (Mandal et al. 2006). Metal nanocrystal synthesis through microbial process is another very promising aspect with importance in metal bioremediation and synthesis of nanoparticles for diverse applications.

2 Metal-Tolerant Microbes

A plethora of microorganisms capable of efficiently degrading toxic compounds in the environment have either been isolated or engineered. One of the prominent bacteria which exhibits extreme radiation resistance is *Deinococcus radiodurans*. It was first discovered in 1956 by Arthur W. Anderson while trying to sterilize meat by irradiating it with gamma radiation (Anderson et al. 1956). For many years, *D. radiodurans* has fascinated biologists by its extraordinary resistance to ionizing radiation. This bacterium, as a polyploid, can withstand radiation exposures of up to $\sim$17,000 gray (Gy) (Daly et al. 1995, 1996, 1997). *D. radiodurans* also dominate the arid environments over other less resilient species by their capacity to regrow after rehydration. Besides UV and IR, *D. radiodurans* is resistant to lethal and mutagenic agents like mitomycin C (Sweet and Moseley 1976), an antibiotic known to cross-link DNA.

Genome sequence of the highly IR-resistant *D. radiodurans* reveals the same number and types of DNA repair proteins as the IR-sensitive bacteria (Makarova et al. 2001, 2007). Following irradiation with lethal doses of IR, radiation-resistant organisms suffer from similar levels of genomic damage as the sensitive ones. This is due to the ability of the resistant strains to survive the formation of hundreds of IR-induced double-strand breaks (DSBs) per genome (Argueso et al. 2008; Gladyshev and Meselson 2008). Studies have shown that a highly IR-sensitive mutant of *D. radiodurans* that contains a mutated DNA polymerase I gene (polA) was fully restored by expression of the corresponding gene of the IR-sensitive *Escherichia coli* (Gutman et al. 1994) The enzymes that mediate DNA repair in *D. radiodurans* are, therefore, probably not unique. Surprisingly, the mechanisms of IR resistance in *Deinococcus* spp. remain unclear along with their unique ability to resist desiccation (Cox and Battista 2005) and UV radiation (Gutman et al. 1994; Minton 1994).

D. radiodurans has been studied for its ability to detoxify or immobilize metallic pollutants. This was made possible by genetic engineering to obtain radiation-resistant organisms that can simultaneously detoxify metals. The *merA* gene encodes mercuric ion reductase that reduces highly toxic, thiol-reactive mercuric ion, Hg(II), to much less toxic and volatile Hg(0) (Schottel 1978; Summers 1986). The *merA* locus from *E. coli* was cloned into *D. radiodurans* to confer both metal resistance and metal-remediating capabilities. In highly irradiating environments, cells that expressed the merA protein were better protected from the effects of Hg(II) than the wild-type counterparts. Cr(VI), a potent carcinogen, is another heavy metal commonly found in radioactive waste sites. In this case as well, genetically engineered *D. radiodurans* capable of reducing Cr(VI) to Cr(III) was preferentially used for rendering it non-mutagenic and non-carcinogenic (Brim et al. 2006). In general, the ability of a microorganism to resist the toxic effect of metals is frequently associated with its ability to transform those metals into less toxic chemical states.

The limitations associated with *D. radiodurans* for in situ bioremediation of nuclear waste sites are the requirements to genetically engineer the bacterium to acquire toxic metal resistance and bioremediating capabilities. The culturing of this bacterium also requires a constant supply of carbon nutrient source and is therefore prone to contamination. The highly radiation-resistant eukaryote counterpart of *D. radiodurans* is found in the form of a microalga, *Coccomyxa actinabiotis* (Rivasseau et al. 2013). It can withstand ionizing radiation doses up to 20,000 Gy with half the population able to survive at 10,000 Gy. Metabolic activity of the cell is marginally affected by radiation doses up to 10,000 Gy and a complete recovery of cellular functioning within a few days. This unique microalga also has the capacity to fix radionuclides such as ^{238}U, ^{137}Cs, ^{110}Ag, ^{60}Co, ^{54}Mn, ^{65}Zn, and ^{14}C via metabolically inactive and active processes even in highly radioactive environments. The main advantage of using photosynthetic organisms is the minimal requirement for energy and culture media, which directly alleviates the problem of bacterial contamination. This newly discovered organism therefore offers great potential for the bioremediation of highly toxic radioactive wastes. Detailed studies with respect to elucidating its metabolic activity and its capability to remediate radionuclides are not only necessary but also inevitable.

Sulfate-reducing bacteria (SRB) are nonpathogenic anaerobic prokaryotes known for their non-photosynthetic activity to generate ATP through electron-transfer-coupled phosphorylation. During this process, SRB uses sulfate as the terminal electron acceptor for respiration of hydrogen to produce sulfide. The sulfide produced is highly reactive and toxic, and therefore, SRB are able to cause severe corrosion of metals in a water system by producing enzymes which can accelerate the reduction of sulfate compounds to hyrdrogen sulfide (Little 1998; Beaton 2007). SRB are used in several in situ technologies like in acid mine drainage (AMD). Extensive mining activity is responsible for changing the basic property of water. When pyrite-containing rocks come into contact with surface water or groundwater, under oxidizing conditions, these rocks produce sulfuric acid and dissolved iron. This acidic water in turn dissolves other metals contained in the rock, resulting in low pH, metal-bearing water known as AMD, or acid rock drainage (ARD). Carbonate minerals may neutralize the acidity and bring the pH to approximately 7.0 to give rise to neutral mine drainage. SRB are used in AMD treatment with the purpose of producing sulfides (for metal sulfide precipitation) and generating alkalinity at the same time.

Microbe-mediated sulfate reduction coupled with organic matter (represented by CH_2O) oxidation forms the chemical basis of SRB remediation

$$2CH_2O(aq) + SO4^{-2} + H^+ \rightarrow H_2S + 2HCO_3$$

It also involves the chemical reaction of metal (Me) precipitation:

$$H_2S + Me^{+2} \rightarrow MeS + 2H^+$$

Precipitation of cadmium, copper, iron, lead, mercury, nickel, and zinc is facilitated by the formation of respective metal sulfides. In addition, arsenic, antimony, and molybdenum form more complex sulfide minerals (Figueroa 2005).

Co-precipitation with other metal sulfides can also be achieved for metals such as manganese, iron, nickel, copper, zinc, cadmium, mercury, and lead (Figueroa 2005). Other SRB species are known to reduce certain metals to a more insoluble form, like reduction of uranium (VI) to uranium (IV) (Spear et al. 2000). Sulfate reduction by SRB also consumes acidity, as a result of which there is an increase in the pH. The above precipitation reactions for metal hydroxides are facilitated by increasing the pH (Gadd 2004).

SRB are known to have a major negative economic impact on the petroleum industry because of their involvement in biocorrosion of ferrous metals in anaerobic environments (Hamilton 2003). Hydrocarbons in petroleum (e.g., benzene, toluene, ethylbenzene, xylenes, naphthalene, phenanthrene, and alkanes) may also serve as electron donors in the normal metabolism of SRB resulting in sulfide production. This biogenic sulfide production typically results in metal corrosion and reservoir souring. In addition, it can also result in the acidulation and plugging of petroleum reservoirs and biocorrosion of metal surfaces of pipelines and tanks (Nemati et al. 2001). Due to the explosive nature of the sulfide, this may pose a risk at high concentrations. The accumulation of SRB biomass thus causes a reduction in the oil recovery (Muyzer and Stams 2008). The need to control or inhibit the growth of SRB in petroleum industries is usually achieved by biocide dosage (Korenblum et al. 2010). Though effective, the inherent problems associated with biocides are the occurrence of antimicrobial resistance (Stewart and Costerton 2001; Fraise 2002), the residual concentration, toxicity, and persistence of biocides in industrial effluents. Alternative strategies for SRB control are therefore of great interest to the petroleum industry (Korenblum et al. 2013).

Remediation of radionuclide or radioactive wastes through microbial processes is an emerging field of research. It has been suggested by current researches that improper treatment approaches can lead to negative impacts on environment and biodiversity, which may even increase distribution of radioactive materials (e.g., wind-aided transport of plutonium-contaminated soil) (Whicker et al. 2004). Microbial consortium is a biological tool widely used for the remediation of pollutants, consisting of several species of microorganisms in the form of bioflocculant. Biofilms produced by microbes, which exist predominantly in natural environments ($\sim$99 %) (Costerton et al. 1995), have the capability to immobilize metals. The different mechanisms adopted by biofilms to immobilize metals or radionuclides are as follows: (1) biosorption to cell components or extracellular polymeric substances (EPS), (2) bioaccumulation, (3) precipitation by reaction with inorganic ligands such as phosphate, and (4) microbial reduction of soluble metal to insoluble form (Gorby and Lovley 1992; Merroun et al. 2003; Renninger et al. 2004). Microbial activity can influence the release of radionuclides by altering bulk pore water chemistry (especially pH and redox reaction), by producing organic complexing ligands or by direct accumulation onto or into cells (West et al. 2002). Microbes can also cause corrosion and hence potentially affect the longevity of the metal waste containers in a repository (Stroes-Gascoyne et al. 2007).

3 Bioremediation: Plant–Microbe Interaction Perspective

The concept of using plants to clean up the environment has generated considerable interest in the last few decades. With the discovery of some plant that has high metal-accumulating capacity (hyperaccumulators) such as *Thlaspi caerulescence* and *Alyssum murales,* cleaning up of metal-contaminated sites using these plants seems like a promising strategy. Metal accumulation in plant biomass constitutes a subclass of phytoremediation called phytoextraction (Raskin and Eansley 2000). Approximately 400 plants have been identified so far which have potential for phytoextraction. Plants species such as *Thlaspi* sp and *Alyssum* spp. from the family Brassicaceae, *Viola calaminaria* and *Astragalus racemosus* from Violaceae and Leguminosae have been found to accumulate high concentration of heavy metals and radionuclides (Negri and Hinchman 2000; Reeves and Baker 2000). Metal-accumulating phenotype in plants is a complex mechanism that requires a concerted effort of tolerance, translocation, and sequestration of targeted metal/s (Hall 2002; Eapen and D'Souza 2005). Understanding the working mechanism of these areas will help enable or improve the metal-accumulating property in hyperaccumulator or even non-accumulating plants. There have been efforts to understand the mechanism of metal accumulation in potential candidates like *T. caerulescence* and other members of Brassicaceae (Baker et al. 1994; Kramer et al. 1996; Salt et al. 1999; Bert et al. 2000; Zhao et al. 2002; Milner and Kochian 2008). However, naturally occurring hyperaccumulators lack certain qualities such as large biomass, fast growth, and habitat incompatibility which limit their use in phytoremediation (Eapen and D'Souza 2005; Kotrba et al. 2009). The success of hyperaccumulation as a mean of cleaning up metal contaminated soil relies on the ability of these plants to tolerate high concentrations and wider metal resistant properties, possessing efficient transport mechanism for metal uptake to accumulation in deep or wide spread roots and aerial portions of the plant that can be easily harvested (Eapen and D'Souza 2005; Kotrba et al. 2009).

Another important aspect of phytoremediation is the relationship of plants with microorganisms existing in the rhizosphere or within the plants itself (endophytes) (Glick 2003, 2010; Kavamura and Esposito 2010; Ma et al. 2011). Plant–microbe interactions are well-known relationships which have been studied thoroughly in laboratory and field studies. Hence, there is no surprise that plants and microbes existing in metal-contaminated site also use this relationship to thrive in stressful environment (Tokala et al. 2002; Gray and Smith 2005). Microorganisms like bacteria are specialists in dealing with metals as they have existed together long before any other higher life forms. Hence, microbes are better adapted and possess well-organized mechanism to deal with the presence or invasion of toxic metals. The various strategies that bacteria utilize in order to negate the presence or increase concentrations of metals include the efflux of metal by different transporters (Nucifora et al. 1989; Solioz and Odermatt 1995), complexation inside the cell (Silver 1996; Robinson 2008), bioprecipitation, and reduction to a less toxic state (Bosecker 1997) (Fig. 1). Bacteria existing in metal-contaminated site can

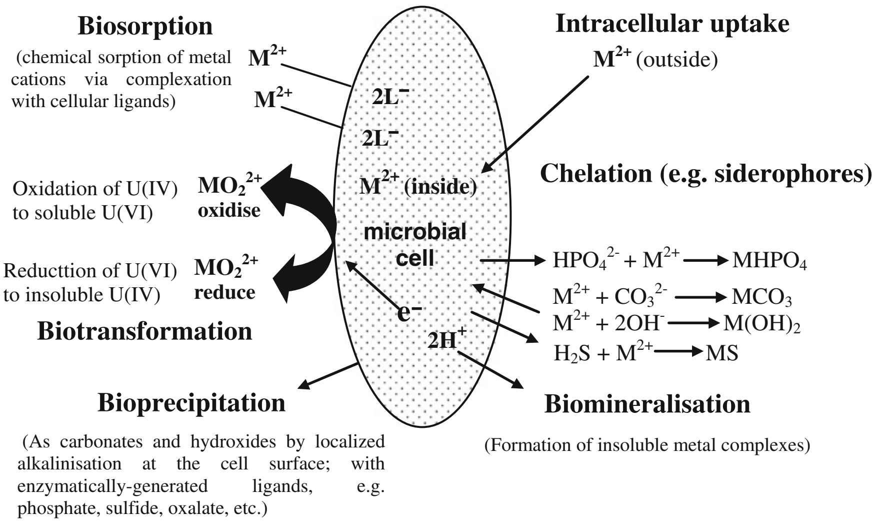

Fig. 1 Diagrammatic representation of the mechanisms of metal/radionuclide–microbes interaction (adapted from Geissler 2007)

influence the physicochemical properties of their habitat including metal(s) in more than one ways.

Bacterial communities have been known to solubilize or precipitate metals in soil, which in turn affects the bioavailability of metals. The bacterial capacity to change the availability of metal in soil can affect plants either by solubilizing the metals so that plant can easily absorb the metals or by precipitating the metals, affecting the survival of plants. Besides changing the bioavailability of metal(s), bacteria can influence the efficiency of phytoextraction by nitrogen fixation and secreting plant growth-promoting hormones such as IAA, siderophore, etc. (Glick 2010; Ma et al. 2011). Plants on the other hand secrete nutrients such as amino acids, sugars, and other metabolites from the roots, which nourish different bacterial species in the rhizosphere.

4 Metagenomics of Metal-Contaminated Sites

The existence of plant–microbe interactions in metal-contaminated site is irrefutable, and various studies have been carried out to understand this relationship (Sriprang et al. 2003; Kuiper et al. 2004; Wu et al. 2006). Moreover, the success of phytoremediation does not depend on plant alone but also on its interaction with the microorganisms in the rhizosphere (Whiting et al. 2001). Understanding the microbial communities existing in metal-contaminated sites is a prerequisite for understanding this relationship. Culturable bacteria have been studied in metal- and radionuclide-contaminated site where diverse groups of bacteria have been isolated and identified (Roane and Kellogg 1996; Selenska-Pobell et al. 2001a, b; Shelobolina et al. 2004; Nedelkova et al. 2007; Islam and Sar 2011; Kumar et al. 2013a). However, culture-dependent methods do not give the true diversity and types of microorganism as ~99 % of bacteria cannot be cultured in laboratory (Pace 1997; Torsvik and Øvreås 2002). With the improvement in metagenomic studies, total bacterial communities existing in metal- and radionuclide-contaminated sites have been explored (Selenska-Pobell et al. 2001a, b; Satchanska et al. 2004; Islam and Sar 2011; Kumar et al. 2013a). This method allows a better understanding on the existing relationship of these bacterial communities with the plant species in that habitat. Comparative metagenomics have been carried out to study the effects of heavy metals on the diversity of bacterial communities. Bacterial communities' structure in uranium deposits has also been studied using both culture-dependent and culture-independent techniques to obtain baseline knowledge on the bacterial communities prior to any mining activities (Kumar et al. 2013b). Similarly, bacterial communities have been explored in uranium-mining sites using both culture-dependent and culture-independent methods. The rhizosphere tends to harbor diverse group of microorganisms as compared to the bulk soil. Hence, a comparative study of bacterial species between the rhizosphere and the bulk soil provides an idea about different bacterial species that contribute to the well-being of the plant(s). Bacterial species in the rhizosphere of hyperaccumulators plants such as *T. caerulescence, A. murales,* etc., have been studied and identified (Gremion et al. 2003). Besides the rhizosphere of hyperaccumulators, bacterial communities in the rhizosphere of pioneer plants in metal-contaminated sites have also been explored (Navarro-Noya et al. 2010). Metagenomics has also been used to compare the effects of different metals on the diversity of bacterial communities (Sobolev and Begonia 2008; Gołębiewski et al. 2013). Besides understanding the community structure, metagenomics has also been in use to understand the different metabolism, evolution, and adaptation of microbial communities in different habitats. Functional metabolic markers such as *nirS, nirK, dsrAB, amoA, pmoA,* etc., have been used to understand the dominant metabolic activities in radionuclide contamination sites (Hemme et al. 2010). Similarly, genes encoding for metal resistance were found to be prevalent and disseminated among those microorganism in metal-contaminated sites (Coombs and Barkay 2004; Martinez et al. 2006; Nongkhlaw et al. 2012) An in-depth and comprehensive study on the microbial communities and its function is very important before any bioremediation practice is established, and metagenomics is an important approach to achieve that goal.

5 Transgenic Metal-Tolerant Plants

The inherent property of some plants to accumulate metal(s) in their biomass has generated and opened new scope for heavy metal remediation. Plants with the capacity to accumulate 50–500 times metal in their biomass as compared to their counterpart growing in the same habitat are termed as hyperaccumulators and considered potent candidates for use in phytoremediation.

The success of hyperaccumulation as a means of cleaning up metal contaminated soil depends on various factors like metal tolerance capability, efficient transport mechanism, high biomass in aerial portion of the plant etc. So far, such ideal plants have not been discovered or do not exist. However, genetic engineering can be used to optimize the existing potential of hyperaccumulators or non-accumulators by introducing new traits from other sources.

With the increased knowledge in plant genetics procedures and metal-tolerant plants with established genetic makeup, *B. juncea, Helianthus annuus,* and *Nicotiana glaucum* appear good candidates for genetic engineering for the purpose of phytoextraction (Eapen and D'Souza 2005; Kotrba et al. 2009). Understanding the mechanism that involves in metal accumulation is very important before genetic manipulation. The ability of plants to accumulate metal(s) in their biomass involves well-organized mechanism that includes metal uptake from the soil, translocation to target compartments, and sequestration. Genetically engineered plants for phytoremediation usually involve the introduction of metal-tolerating genes from other plants, but genes from human, animal, fungi, and bacteria have also been used to improve metal accumulation (Eapen and D'Souza 2005; Kotrba et al. 2009). Genes that encode metal sequestration factors such as metallothioneins (Misra and Gedamu 1998; Evans et al. 1992) and phytochelatins (Zhu et al. 1999a, b; Harada et al. 2001) from other sources have been introduced in plants. Constitutive expression of genes encoding metallothioneins from mouse, human, and Chinese hamster in *Nicotiana tabaccum*, *Brassica oleracea,* and *Arabidopsis thaliana* showed increased Cd^{2+} tolerance but reduced metal accumulation in shoots. Similarly, genes from bacteria and fungi have been cloned and expressed in plants cells for obtaining metal-tolerant phenotype (Table 1). Expression of yeast *CUP1* increased Cd^{2+} tolerance in *B. oleracea,* but there is no increased accumulation. However, expression of yeast CUP1 increased Cu^{+} but not Cd^{2+} accumulation in leaves of *N. tabaccum*. A more promising Cd^{2+} accumulation in transgenic line was seen with recombinant HisCUP. Improved Hg^{2+} accumulation was also seen in *A. thaliana* transgenic expressing bacterial Hg^{2+} binding protein, MerP. In addition to the improvement of metal accumulation trait, plants also need to combat the oxidative stress known to be induced by heavy metals. Hence Glutathione synthesis genes from bacteria and fungi have been introduced and overexpressed in plants with the aim of increasing metal tolerance and sequestration (reviewed in Eapen and D'Souza 2005; Kotrba et al. 2009). Maintenance of metal homeostasis carried out by various metal-transporting proteins is another important aspect for metal tolerance and accumulation. Similarly, metal transporters from bacteria and fungi have been cloned and expressed in plants. Zinc/Lead/Cadmium metal-transporting P_{IB}-ATPase (ZntA) from *E. coli* has been successfully expressed in *A. thaliana* (reviewed in Eapen and D'Souza 2005; Kotrba et al. 2009). Similarly, mercury-resistant genes such as *merA*, *merB,* and *merC* have been successfully cloned in plant species

Table 1 Examples of transgenic plants expressing bacterial/fungal genes

Transgenic plant	Source	Gene name	Altered phenotype	References
Cauliflower	Yeast	CUP-1	Cd tolerance	Hasegawa et al. (1997)
Tobacco	Yeast	CUP-1	Cu tolerance	Thomas et al. (2003)
Indian Mustard	*E. coli*	γ-Glutamylcysteine synthetase	Cd tolerance	Zhu et al. (1999b)
Tobacco	Yeast	FRE1 and FRE2	Fe content	Samuelsen et al. (1998)
Rice	Bacteria	Citrate synthase	Al tolerance	De la Fuente et al. (1997)
Indian Mustard	Bacteria	Arsenate reductase g-glutamylcysteine synthetase *gsh1* and *arsC*	As tolerance	Dhankher et al. (2002)
Arabidopsis thaliana	*E. coli*	*zntA*	Cd and Pb tolerance	Lee et al. (2003)
Arabidopsis	Yeast	YCF-1	Cd and Pb tolerance	Song et al. (2003)
B. juncea	*E. coli*	*gsh1*	Cd accumulation	Zhu et al. (1999b)
Populus	*E. coli*	*gsh1*	Cd, Zn, Cu, and Pb accumulation	Bennett et al. (2003)
A. thaliana	*Acidithiobacillus ferrooxidans*	*merC*	Hg^{2+} accumulation	Sasaki et al. (2006)
A. thaliana	*S. cerevisiae*	GSH1	Cd and As accumulation	Guo et al. (2008)
Lycopersicon esculentum	*Enterobacter cloacae*	ACC deaminase	Cd, Co, Cu, Ni, Pb, and Zn accumulation	Grichko et al. (2000)
Tobacco	*Neurospora crassa*	Zn transporter gene	Zn accumulation	Dixit et al. (2010)
Tobacco	*Neurospora crassa*	Cu transporter (*tcu-1*)	Cu acquisition	Singh et al. (2011)
A. thaliana	Bacterial	*merC*	Cd accumulation	Kiyono et al. (2012)

resulting in increased tolerance and accumulation of mercury by the transformed plant. Very few reports are available on the use of metal transporters from bacterial origin for making metal-tolerant transgenic plants except for those mentioned above.

Negri and Hinchman (2000) have reported the use of the plants for treatment of ^{3}H, U, Pu, ^{137}Cs, and ^{90}Sr. Phytoextraction removes radionuclides from soil without destroying the soil structure having limited impact on soil fertility for the treatment of large areas of low-level contamination, and its success depends on the bioavailability of radionuclides in soil, on the rate of uptake by plant roots and transportation efficiency of the vascular system of plants (Slavik Dushenkov 2003).

6 Conclusion

Microbial bioremediation is the process by which microbes degrade or transform hazardous organic compounds into non-toxic products. Since the plethora of microorganisms teeming in nature are not capable of degrading all toxic compounds, especially xenobiotics, the use of genetically modified organisms forms an indispensable part of bioremediation approaches with the advancement in genetic manipulation. Although genetically engineered microbes are quite promising, their implementation for in situ bioremediation still requires additional routes for developing safe steps to environmental cleanup. One of the major challenges is to optimize conditions and procedures for sustained and effective bioremediation in the presence of toxic metals and organic compounds. Conditions are created to enhance microbial activity for in situ biostimulation or bioaugmentation which may disrupt the natural microbiota. Various issues are to be dealt with to enhance the metabolic activity while maintaining the required growth conditions such as pH, temperature, the levels of contaminants and nutrients, etc. Due to the complex nature of interactions between microorganisms and radionuclides, it is far from easy to understand the wide range of environments these organisms inhabit. To study the molecular mechanisms and identify novel genes, proteins, and enzymes involved in the bioremediation of radionuclides necessitates the study toward the structural and functional interactions between proteins and other metabolites. Therefore, identification of potential genes and proteins involved in the metabolism of radionuclides can be achieved by advanced genomics and proteomics techniques. With the recent advances in next-generation sequencing, genomics, and proteomics, it has become possible to check for the expression of proteins and enzymes of interest with the potential for radionuclide resistance. Genome-wide transcriptome analysis can further provide detailed insight into better understanding of the metabolic pathways and the physiology of the microorganisms.

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Metabolism of ^{14}C-Containing Contaminants in Plants and Microorganisms

Giorgi Kvesitadze, Gia Khatisashvili and Tinatin Sadunishvili

Abstract The most important researches of organic contaminants metabolism in plants and microorganisms using ^{14}C-labeled compounds are reviewed. The data that indicate on biodegradation and full detoxification (mineralization) of organic contaminants, such as aliphatic and monoaromatic hydrocarbons and their derivatives, polycyclic aromatic hydrocarbons, organochlorine pollutants, and, 2,4,6-trinitrotoluene, in microorganisms and to lesser extent in plants are presented.

Keywords Phytoremediation · Mineralization · Aliphatic hydrocarbons · Monoaromatic hydrocarbons · Polycyclic aromatic hydrocarbons · Organochlorine contaminants

Contents

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1 Introduction

Radiocarbon, ^{14}C is the natural radioactive isotope of carbon (half-life of 5,730 years), which is formed in the upper layers of the atmosphere as a result of cosmic rays action. After production, the ^{14}C atoms react to form ^{14}CO, which subsequently oxidizes to $^{14}CO_2$. The gas mixes rapidly and becomes evenly distributed throughout the atmosphere. Radioactive carbon dioxide also dissolves in water and thus permeates the oceans, but at a slower rate (Ramsey 2008).

Radiocarbon is beta-emitter but ^{14}C itself does not represent a pollutant, as its natural content in compounds is very low (natural abundance is 1 part per trillion). Labeled with ^{14}C organic pollutants are widely used in phytoremediation researches, as ^{14}C presence allows to follow pollutants metabolism in plants, by means of autoradiography monitor their translocation in plant organs and distribution among tissues and separate ultracellular organelles. Application of ^{14}C-labeled compounds gives the most trustworthy and convincing data on whether full detoxification (mineralization) of organic pollutant takes place or not during the process of phytoremediation.

The chapter describes the most important data obtained as a result of study of ^{14}C-labeled organic pollutants metabolism in plants and microorganisms.

2 Metabolism of ^{14}C-Labeled Aliphatic and Monoaromatic Hydrocarbons and their Derivatives

As a result of incubation of numerous plants (55 representatives of annual and perennial plants) with ^{14}C-labeled carbohydrates, it was demonstrated that all of them uptake and metabolize alkanes and arenes with different intensities (Durmishidze and Ugrekhelidze 1975; Durmishidze et al. 1974a, b). Benzo[a]-pyrene and benz[a]anthracene are actively uptaken, transported, and metabolized by plants (Devdariani 1988; Devdariani and Durmishidze 1983; Devdariani and Kavtaradze 1979a, b; Devdariani et al. 1979a, b; Müller 1976). The products of transformation of hydrocarbons uptaken by leaves flow along the stem to the roots and from the roots the intermediates of absorbed and metabolized hydrocarbons migrate to leaves (Korte et al. 2000).

By using labeled with ^{14}C compounds, it has been shown that ryegrass (*Lolium perenne* L.) has the capacity of taking up radioactive C_1–C_6 and C_8 monatomic alcohols, benzyl alcohol, C_1–C_2 aldehydes, acetone, acetaldehyde, C_1–C_6 monocarbonic acids, acetoacetic acid, acetic anhydride, cyclohexane, benzene, toluene, phenol, α-naphthol, naphthalene, and chloroform from the air by leaves (Durmishidze and Beriashvili 1979). It has been established that these compounds undergo oxidative degradation in ryegrass leaves, resulting with destruction of carbon skeleton, cleaving cyclic and bicyclic rings, and labeled carbon atoms of tested xenobiotics are incorporated into the common metabolites of the cell such as: sugars (glucose, fructose, sucrose, raffinose), organic acids (malic, succinic, fumaric, citric, glycolic, glyoxylic, malonic, muconic, and other), amino acids (threonine, serine, glutamic and aspartic acids, lysine, alanine, phenylalanine valine, tryptophan, methionine, leucine, proline, glycine, etc.), and biopolymers. The authors suggest that as a result of hydroxylation, decarboxylation, and other transformation of xenobiotics intracellular concentration of $^{14}CO_2$ increased that induce photosynthetic formation of sugars and other intracellular compounds.

The experiments with ^{14}C-labeled hydrocarbons proved that sterile plant seedlings, placed in an atmosphere containing low-molecular mass alkanes (C_1–C_5) or cyclohexane, uptake these compounds, exposing their molecules to deep oxidative transformations to $^{14}CO_2$ (Durmishidze and Ugrekhelidze 1967, 1968a, 1975). In a plant cell, these hydrocarbons are oxidized and form the corresponding carbonic acids. On the basis of identified intermediate products, it was concluded that these alkanes undergo monoterminal oxidation, with formation of the corresponding primary alcohols, followed by oxidation to carboxyl acids, while cyclohexane oxidizes via ring cleavage (Korte et al. 2000; Ugrekhelidze 1976). The emission of $^{14}CO_2$ in the dark during this process serves as evidence for the occurrence of mineralization and can be easily measured (depending on the time of exposure, the percent of mineralization was found to be as high as 30 %). Consequently, organic and amino acids are among the end products of this transformation, and they can be used for further cell metabolism (Penner and Early 1973).

The transformation of [^{14}C] methane in higher plant cells is carried out by primary hydroxylation and successive forming of methanol, formaldehyde, and formic acid (Kvesitadze et al. 2006; Ugrekhelidze 1976). The oxidation of [1,2-^{14}C] ethane at one-terminal carbon atom leads to the formation of acetyl-CoA, which in turn is able to participate in the Krebs cycle. Concerning hypothesis of monoterminal oxidation of ethane: if ethane was oxidized at both terminal carbon atoms, instead of one, the carbon atoms originating from ethane would be incorporated into glycolic, glyoxalic or oxalic acids, but the ^{14}C carbon atoms originating from ethane are incorporated basically into succinic and fumaric acids (Ugrekhelidze 1976).

Based on the identified low-molecular mass degradation ^{14}C-products (succinic, fumaric, malonic, malic, and citric acids), which are formed during mineralization of [1–3-^{14}C] propane to $^{14}CO_2$ by plants, it is suggested that propane is also oxidized monoterminally. The primary oxidation of propane at one-terminal carbon atom leads to the formation of [1–3-^{14}C] propionic acid. This intermediate consequently transforms to malonyl-CoA as a result of β-oxidation. Last product undergoes decarboxylation resulting in the formation of acetyl-CoA (Kvesitadze et al. 2006; Ugrekhelidze 1976). Acetyl-CoA is transferred to carboxyl groups of succinic acid that can be incorporated into the Krebs cycle.

The presence of [^{14}C] fumaric, glycolic, and malic acids and the absence of labeled γ-isobutyric and succinic acids among radioactive intermediates forming as a result transformation of [1–4-^{14}C] butane indicate on monoterminal mechanism of butane mineralization in plants (Ugrekhelidze 1976). The incorporation of butane carbon skeleton in Krebs cycle is possible via β-oxidation of formed butyric acid to C_2-acids, e.g., to glycolic acid, identified as one of radioactive metabolite of butane.

The tea (*Thea sinensis*) seedlings, grown in an atmosphere containing [1–5-^{14}C] pentane, release $^{14}CO_2$ (approximately 30 % from total radioactivity) after being transferred to a pentane-free atmosphere. The radioactive label of absorbed pentane is observed in the low-molecular mass compounds. Among them, nonvolatile organic acids (fumaric and succinic acids) and amino acids (alanine and glutamic acid) were identified, but the sugar fraction remained nonradioactive. The radioactive label was almost equally inserted in organic acids (fumaric and succinic acids) and amino acids (the most radioactivity was found in alanine). Absence of the labeled carbon atoms in the sugars can be explained by the fact that being in the dark, photosynthesis and, correspondingly, the biosynthesis of sugar does not take place. The presence of the carbon label of pentane in components of the Krebs cycle indicates that [1–5-^{14}C] pentane metabolism in the plant cells proceeds via monoterminal oxidation as well as in case of C_1–C_4 alkanes, but oxidation of butane leads to forming of valeric acid and its successive conversion to acetyl-CoA, which can be inserted into the Krebs cycle (Durmishidze and Ugrekhelidze 1968b; Ugrekhelidze 1976; Ugrekhelidze and Durmishidze 1984; Varazashvili and Pruidze 2005). The above described transformation of pentane can be sketched in Fig. 1.

Obviously, the longchain alkanes also are subjected to oxidative transformations in plants and the steps of their degradation are similar to conversion of short chain alkanes. For instance, after 40 min of incubation of leek (*Allium porum* L.), leaves with an emulsion of exogenous [^{14}C] octadecane in water, 9.6 % of the total label is detected in esters, 6.4 % in alcohols, and 4 % in organic acids (Cassagne and Lessire 1975).

The evolution of $^{14}CO_2$ during incubation of plants with [1-^{14}C] cyclohexane indicates that the ring of this hydrocarbon is cleaved with the formation of aliphatic products. The major component among them is succinic acid (Ugrekhelidze 1976). The incorporation of radioactive carbon atoms in tyrosine and phenylalanine is also observed. It was supposed that in plants the first step of cyclohexane transformation is its hydroxylation into cyclohexanol. The inferred scheme of cyclohexane metabolism in plants is in Fig. 2.

As is seen from the scheme (Fig. 2), in the initial stage, cyclohexane undergoes oxidation to unsaturated cyclic intermediates with oxo- or hydroxyl-groups. In the next stage of metabolism, these intermediates form cyclohexene-3-diol-1,2, which is oxidized with cleavage of carbonic cycle and is transformed into adipinic acid. This metabolite can form fumaric acid and thus, incorporates into general metabolism of organic acids in plant cell.

The experiments with using ring-labeled arenes (^{14}C-benzene and ^{14}C-toluene) and avocado (*Persea americana*) fruit demonstrate that hydrocarbons are transformed to a series of compounds, toluene to a greater extent than benzene. After 4 h of exposure time, both arenes formed a little amount of $^{14}CO_2$ (Jansen and Olson 1969). It have been established that vapors of [1–6-^{14}C] benzene and [1-^{14}C] toluene penetrated in plants (maple (*Acer campestre*), apple (*Malus domestica*) and

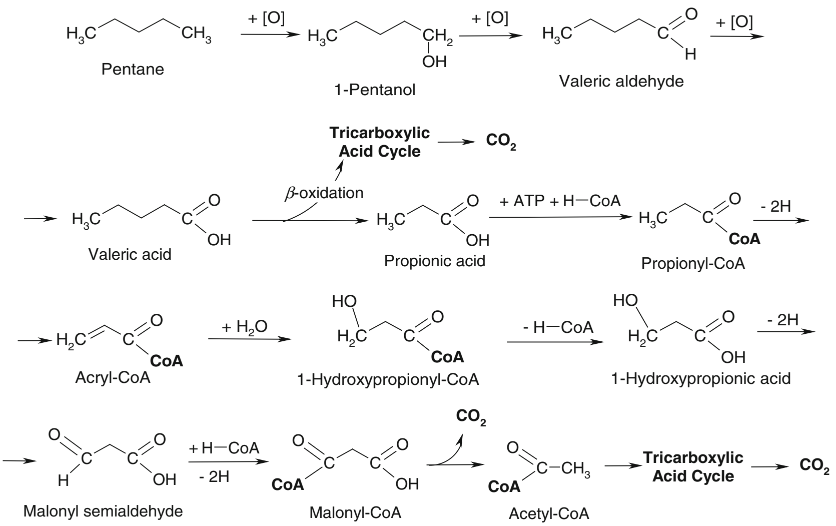
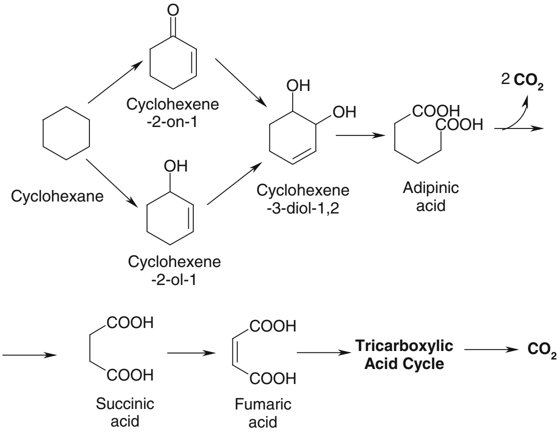


Fig. 1 Hypothetic pathway of pentane metabolism in the higher plant cells

Fig. 2 Oxidative degradation of cyclohexane in plants



vine (*Vitis vinifera*)) through hypostomatous leaves from both sides, whereas hydrocarbons are more intensively up taken by the stomatiferous side and more actively taken up by young leaves (Kvesitadze et al. 2006; Ugrekhelidze et al. 1997). Transformation of these radioactive arenes in leaves includes the aromatic ring cleavage and labeled carbon atoms are mainly incorporated into nonvolatile organic acids (basically into muconic and fumaric acids in case of benzene, and into muconic and malic acids in case of toluene), while their incorporation into amino acids (particularly, into tyrosine and phenylalanine in case of benzene, and into tyrosine and aspartic acid in case of toluene) is less intensive. It has been shown that intact spinach (*Spinacia oleracea*) leaves mineralize the absorbed [1–6-^{14}C] benzene and

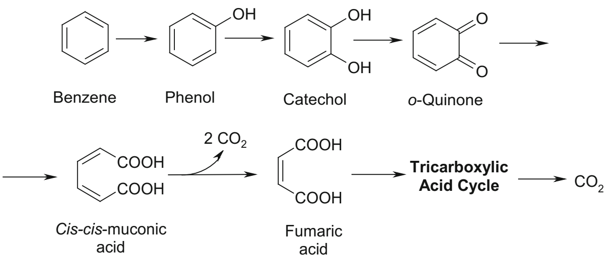


Fig. 3 Oxidative degradation of benzene in plant cells according to Kvesitadze et al. (2006)

[1-^{14}C] toluene to $^{14}CO_2$, and this process is strongly stimulated in light. Oxidation of [1–6-^{14}C] benzene by spinach chloroplasts or by enzyme preparation from spinach leaves is almost completely inhibited by chelating of copper ions and slightly by chelating of iron ions. Benzene oxidation by enzyme preparation is significantly stimulated by NADH and NADPH; in their presence, [1–6-^{14}C] phenol, as hydroxylation product of the benzene, is formed. It is worth noting that the labeled phenol was isolated from sterile seedlings of maize, pea, and pumpkin incubated on the solution of [1–6-^{14}C] benzene.The phenol was present in tissues in negligible amounts, though the degree of benzene label incorporation into aliphatic products was much higher (Korte et al. 2000; Ugrekhelidze et al. 1977). It is supposed that the first step of oxidative transformation of benzene in plant leaves is hydroxylation via enzyme containing copper as the prosthetic group (Ugrekhelidze et al. 1997). Further, oxidation of phenol in catechol leads to the aromatic ring cleavage and formation of muconic acid, which subsequently transforms into fumaric acid. The last easily incorporates in tricarboxylic acid cycle, and as a result, full mineralization of aromatic hydrocarbons to carbon dioxide takes place (see scheme in Fig. 3) (Durmishidze et al. 1969, 1974a, b, c). These dicarbonic acids are often found in plants exposed to benzene or phenol. Such cleavage of the aromatic ring is typical for endogenous substrates (Tateoka 1970). If toluene degradation performs via similar pathway, labeled α-methylmuconic acid will be identified among the intermediates of [1-^{14}C] toluene transformation in plants. However, such compound, as well as the benzoic acid were not identified (Ugrekhelidze 1976).

It has been demonstrated that [1–6-^{14}C] phenol (hydroxybenzene) penetrated through the roots of mung bean (*Vigna radiata*) and wheat seedlings is coupled to low-molecular-weight peptides, forming phenol–peptide conjugates (Chrikishvilli et al. 2005; Ugrekhelidze et al. 1999). The part of [1–6-^{14}C] phenol absorbed by higher plants is detoxified by oxidative cleavage of the aromatic ring. Thus, the sterile plants absorbing $^{14}C_6H_5OH$ are able to release $^{14}CO_2$ after exposure to darkness; in addition, in tissues of these plants labeled muconic acid and fumaric acid were found (Ugrekhelidze 1976; Ugrekhelidze et al. 1999). Rather specific products of conjugation are produced from pentachlorophenol in soybean (*Glycine max*) and wheat (*Triticum aestivum*) (Sandermann et al. 1991; Schmitt et al. 1985). In these plants, pentachlorophenol is transformed into *β*-D-glycosyl and *O*-malonyl*β*-D-glucosyl conjugates.

The investigations of the fate of different exogenous monatomic phenols in plants show that the main pathway of their transformations is conjugation with the low-molecular mass peptides. For instance, [1-^{14}C] *o*-nitrophenol, [1-^{14}C] 2,4-dinitrophenol, and [1-^{14}C] α-naphthol, after penetration into sterile pea (*Pisum sativum*) seedlings, bind with such peptides (Arziani et al. 1983, 2002). The part of these monatomic phenols is irreversibly bound to proteins via quinone–protein interaction and only a small part are transformed via aromatic ring cleavage. Monatomic phenol with high dissociation constant (dinitrophenol) causes a corresponding stimulation of peptide accumulation in plant tissues. It is also worth noting that in contrast to polyatomic phenols, which are metabolized in higher plants via glycosylation (Glass and Bohm 1971; Pridham 1964), the above mentioned monatomic phenols do not form corresponding glycosides in tissues of investigated plant.

Transformation of labeled benzene derivatives, [1–6-^{14}C] nitrobenzene, ([1–6-^{14}C] aniline, [1-^{14}C] and [7-^{14}C] benzoic acid, in axenic seedlings of maize (*Zea mays* L.), kidney bean (*Phaseolus vulgaris* L.), pea, and pumpkin (*Cucurbita pepo* L.) have been studied (Mithaishvili et al. 2005). After penetration in plants, these pollutants undergo oxidative or reductive transformations, which lead to the cleavage of aromatic ring or to the conjugation with peptides and biopolymers. Ring cleavage is accompanied by formation of labeled organic acids of the Krebs cycle and subsequent emission of $^{14}CO_2$. The analysis of conjugates has been shown that as a result of reduction or hydroxylation of [1–6-^{14}C] nitrobenzene, correspondingly, labeled aniline or *o*-nitrophenol is produced (*p*-nitrophenol was identified in trace amount). Labeled metabolites of [1–6-^{14}C] aniline are involved in the formation of peptide conjugates. Concerning [^{14}C] benzoic acid, this xenobiotic is directly linked to the amino groups of peptides at the expense of own carboxylic group. In other experiments with [1-^{14}C] and [7-^{14}C] benzoic acids, it has been established that after removal of the plants (sterile seedlings of maize and pea) from the labeled benzoic-acid-containing hydroponic medium, the amount of conjugation products gradually decreases and the process is accompanied by the emission of labeled carbon dioxide (Chrikishvili et al. 2006). This indicates that conjugates eventually release their toxic part unchanged, which further undergo mineralization by plant cell enzymes.

Although plants have the inherent ability to detoxify xenobiotics, they generally lack the catabolic pathway for the complete degradation of these compounds as compared to microorganisms (Abhilash et al. 2009). Due to their fast growing ability, much more easily regulated adaptation, fast inductive processes, and the wide spectrum of the enzymes participating in the degradation of organic xenobiotics, microorganisms are much more active detoxifiers when expressing their activity per unit of dry biomass (or in any other way) (Kvesitadze et al. 2006). Such advantages of microorganisms also are revealed in degradation of hydrocarbons. As it will be shown below, researches using ^{14}C-labeled compounds confirmed that microorganisms from different taxonomic groups have capabilities to mineralize wide spectrum of aliphatic alkanes, cycloalkanes, arenes, and their derivatives in both aerobic and anaerobic conditions.

For instance, it has been demonstrated that strain *Rhodococcus* sp. EH831 isolated from the enriched hexane degrading bacterial consortium was able to mineralize approximately half part of the [1–6-^{14}C] hexane into $^{14}CO_2$ (Lee et al. 2010). Among intermediates, the oxidative degradation products of hexane such as alcohols, ketones, and aldehydes are identified.

Entomopathogenous fungi are able to transform [1-^{14}C] *n*-hexadecane into different lipid products, part of which is subsequently utilized for energy formation, and the complete catabolism of hexadecane ended by a significant release of $^{14}CO_2$ (Napolitano and Juárez 1997). The study of the ability of filamentous fungi to degrade crude oil components shows that [1-^{14}C] *n*-hexadecane is being mineralized, not simply transformed to intermediate metabolites (April et al. 1999). [1-^{14}C] Hexadecane was also anaerobically oxidized to $^{14}CO_2$. Molybdate, a specific inhibitor of sulfate reduction, inhibited the hexadecane oxidation (Coates et al. 1996). These results demonstrate that a wide variety of hydrocarbon contaminants can be degraded under sulfate-reducing conditions in hydrocarbon-contaminated sediments.

In some cases, ^{14}C-labeled components of oil hydrocarbons were used for determination of remediation potential of microorganisms. For instance, the rate of utilization of [1-^{14}C] hexadecane was used for estimating the hydrocarbon-degrading potential of bacteria (Walker and Colwell 1976). In experiments, conducted for estimation of aerobic biodegradation potential of the microbial community, contaminated sediments were incubated with ^{14}C-labeled organic compounds (among them [1–6-^{14}C] benzene and [1–6-^{14}C] toluene), and the evolution of $^{14}CO_2$ was measured over time (Aelion and Bradley 1991).

It has been established that the enrichment of halophilic and halotolerant bacteria completely degraded labeled benzene, toluene, ethylbenzene, and xylenes within 1–2 weeks under aerobic conditions. Community structure analysis revealed that *Marinobacter* spp. were the dominant members of the enrichment (Nicholson and Fathpure 2004). Bacterial community from hypersaline soil samples has the capability to use of [1–6-^{14}C] benzene as the sole carbon and energy source, and herewith, 1/3 of the assimilated [1–6-^{14}C] benzene was converted to $^{14}CO_2$ (Nicholson and Fathpure 2005).

Studies with labeled [1–6-^{14}C] benzene and [1–6-^{14}C] toluene showed substantial mineralization of these compounds to $^{14}CO_2$ by the lignin-degrading basidiomycete *Phanerochaete chrysosporium* (Yadav and Reddy 1993a). *P. chrysosporium* was also shown to degrade monatomic phenols (simple phenol and *p*-cresol) (Kennes and Lema 1994). [^{14}C] Benzene can be mineralized in both aerobic and anaerobic conditions (Vogt et al. 2011). Aerobic microbial degradation of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes occurs by means of preliminary hydroxylation and consequent cleavage of aromatic ring, similar to plants (Gibson and Parales 2000; Jindrová et al. 2002; Tao et al. 2004).

Under anaerobic conditions in methanogenic enrichment cultures, amended with ^{14}C-benzene degradation of this compound by formation of $^{14}CO_2$ and $^{14}CH_4$

was demonstrated (Grbic-Galic and Vogel 1987; Vogel and Grbic-Galic 1986). The mass balance showed that less than 6 % of ^{14}C-labeled benzene added was converted to $^{14}CO_2$. In other experiments, more than 90 % of ^{14}C-labeled benzene was mineralized to $^{14}CO_2$ by aquifer-derived microorganisms under strictly anaerobic conditions, by using sulfide-reduced mineral medium (Edwards and Grbic-Galic 1992). It has been demonstrated that the addition of sulfate stimulates anaerobic benzene degradation in methanogenic sediments (Weiner et al. 1998). In experiments with ^{14}C-labeled benzene, more than 90 % labeled carbon of the benzene was released as CO_2 (Burland and Edwards 1999). Complete mineralization of benzene to carbon dioxide and methane were significantly higher under methanogenic conditions (Kazumi et al. 1997; Ulrich and Edwards 2003).

Diverse strains of anaerobic bacteria have been isolated that degrade alkylbenzenes anaerobically, using nitrate, iron(III), or sulfate as electron acceptors (Spormann and Widdel 2000). It has been shown that the denitrifier strain *Azoarcustolulyticus* Tol-4 is capable to anaerobic mineralization of [1–6-^{14}C] toluene: 68 % of ^{14}C was found in carbon dioxide and 30 % in biomass (Chee-Sanford et al. 1996).

Anaerobically, in presence of nitrates, *Dechloromonas* strain RCB completely degrades [1–6-^{14}C] benzene (concentration 160 μM) to $^{14}CO_2$ within 5 days (Coates et al. 2001). This process is nitrate-dependent and involves an initial hydroxylation, subsequent carboxylation, and loss of the hydroxyl group to form benzoate (Chakraborty and Coates 2005). According to suggestions of the authors, all anaerobic benzene degrading microorganisms, regardless of their terminal electron acceptor carry out benzene degradation by this pathway. In addition to nitrate, strain RCB could alternatively degrade benzene both aerobically and anaerobically with perchlorate or chlorate as a suitable electron acceptor (Chakraborty et al. 2005). Also, this strain was capable to anaerobically degrades other monoaromatic hydrocarbons, and toluene and ethylbenzene were completely mineralized to CO_2.

3 Metabolism of ^{14}C-Labeled PAHs

Because of wide spread occurrence and carcinogenic properties, PAH represent one of the most dangerous groups of environmental pollutants.

PAH represent one of the groups of environmental pollutants of great concern. The low solubility in water and the high chemical stability of polycondensed aromatic structure predetermine the recalcitrance of PAHs to biodegradation. Microbial degradation is being the primary route of mineralization of PAHs in soils (Rojo-Nieto and Perales-Vargas-Machuca 2012). However, it is not the only way of biotransformation of PAHs in the environment, since the great number of investigations with using ^{14}C-labeled PAHs demonstrate that higher plants have capacity to uptake and degrade these compounds.

Persistence of the PAHs increases as the number of condensed rings and also depends on the location of the rings in a molecule (Bezalel et al. 1996a, b).

Respectively, the simplest PAH naphthalene is more easily exposed to mineralization. The possibility of naphthalene degradation by bacterial strains under nitrate-reducing anaerobic condition has been confirmed by measuring mineralization of [^{14}C] naphthalene to $^{14}CO_2$ (Bregnard et al. 1996). Similar results are under sulfate-reducing conditions for [^{14}C] naphthalene and [^{14}C] phenanthrene (Coates et al. 1997). It has been demonstrated that microbial mineralization of [^{14}C] naphthalene to labeled carbon dioxide may be coupled to sulfate reduction in aquifer-derived sediments (Bedessem et al. 1997). As much as 66 % of labeled naphthalene was mineralized to $^{14}CO_2$ over 13 days, and molybdate inhibited the intensity of this process by 44 %. By using [^{14}C] naphthalene, it has been established that the abundance of the naphthalene dioxygenase gene *nahAc* was correlated with the aerobic naphthalene mineralization potential in oxic soil layer of petroleum hydrocarbon-contaminated sites (Tuomi et al. 2004).

Some plant species are distinguished by high ability to uptake PAHs from environment (Slaski et al. 2000). In early studies, it has been shown that the absorbed by roots of maize and kidney bean [1,2-^{14}C] benzo(a)pyrene was transported to leaves and some its part undergo biotransformation that was accompanied by the release of labeled carbon dioxide (Ugrekhelidze 1976). Radioactive carbon dioxide as the final product of the oxidation of [9-^{14}C] benzo(a)anthracene was also detected in herbaceous plants ryegrass and alfalfa (*Medicago glutinosa*) (Devdariani and Kavtaradze 1979a, b). Among the metabolites of [7,10-^{14}C] benzo(a)pyrene enzymatic oxidation-labeled 1,6-benzo(a)pyrene-quinone, 6,12-benzo(a)pyrene-quinone, 3,6-benzo(a)pyrene-quinone, 9,10-dihydrodiol-BP, 7,8-dihvdrodiol-benzo(a)pyrene, 4,5-dihydrodiol-benzo(a)pyrene and 3-hydroxo-benzo(a)pyrene are identified (Durmishidze et al. 1979b). In most cases, further oxidation of formed metabolites followed by ring cleavage. It has been also shown that separate organelles isolated from pea seedlings oxidize [7,10-^{14}C] benzo(a)pyrene to carbon dioxide (Devdariani et al. 1979b). Maize, kidney bean, and pumpkin revealed ability to cleavage of [3,4-^{14}C] benzo(a)pyrene B and C rings under sterile conditions by the formation of radioactive organic acids and amino acids and by emission of $^{14}CO_2$ (Durmishidze et al. 1979a). For such PAHs as naphthalene, pyrene, anthracene, and dibenzanthracene, the same kind of transformation is observed (Devdariani 1988). It is supposed that hydroxylation is the primary reaction in the transformation of polycyclic hydrocarbons in plants. The analogous transformation of PAHs was determined in cell suspension cultures (Harms 1975; Harms et al. 1977; Trenk and Sandermann 1978).

The extent of PAHs destruction in the environment is of high importance. It has been shown that partial degradation of PAHs in soil can become a reason of the groundwater pollution with toxic metabolites (Schmidt et al. 2010). Mineralization of labeled metabolites, produced by fungus *Cunninghamella elegans* from [^{14}C] phenanthrene, [^{14}C] fluoranthene, and [^{14}C] pyrene, was compared to mineralization of the parent [^{14}C] PAHs in soil slurries. It was supposed that reduction of lipophlicity and raising bioavailability of the metabolites compared to the parent PAHs would enhance the degree of their mineralization in soil slurries (Schmidt et al. 2010). Unexpectedly, the mineralization of the labeled metabolites was in all cases extremely slow as compared to the mineralization of the parent [^{14}C] PAHs.

Comparing the PAHs-degradation abilities of the microorganisms from different taxonomic groups might be suggested that fungi are distinguished by greatest ability. It has been demonstrated that the white rot fungus *Pleurotus ostreatus* mineralized to labeled carbon dioxide 7.0 % of [^{14}C] catechol, 3.0 % of [^{14}C] phenanthrene, 0.4 % of [^{14}C] pyrene, and 0.19 % of [^{14}C] benzo(a)pyrene by day 11 of incubation. It also mineralized [^{14}C] anthracene (0.6 %) much more slowly (35 days) and [^{14}C] fluorene (0.19 %) within 15 days (Bezalel et al. 1996a, b). In other experiments, this fungal strain degraded [^{14}C] benzo(a)pyrene and 40 % of the compound was removed after one month of incubation. The mineralization degree (estimated by measuring of released $^{14}CO_2$) as compared to unsterile control soil without tested fungal strain increased from 0.1 to 1 % (Eggen and Majcherczyk 1998). Fungal strain *Stropharia coronilla* mineralized approximately 12 % of the added [^{14}C] benzo(a)pyrene in Mn^{2+} supplemented cultures within 6 weeks, whereas only 1 % was evolved as $^{14}CO_2$ in non-supplemented cultures (Steffen et al. 2003).

The increase of bioavailability promotes the biotransformation of PAHs. So, the effects of pig manure compost (PMC) and a nonionic surfactant Tween 80 on the transformation of [^{14}C] pyrene in a soil–plant system (*Agropyron elongatum*) have been studied (Cheng and Wong 2008). The results showed that the mineralization of [^{14}C] pyrene depends on the dissipation degree of PAH in vegetated soil, and the co-addition of Tween 80 and PMC could improve the intensity of both dissipation and mineralization processes.

Plant-microbial interaction is important factor for improving rhizodegradation of PAHs. Thus, plant root extracts of osage orange (*Maclura pomifera*), hybrid willow (*Salix alba* × *matsudana*), or kou (*Cordia subcordata*), or plant root exudates of white mulberry (*Morus alba*) supported 15–20 % benzo[a]pyrene removal over 24 h. Mineralization of [7-^{14}C] benzo(a)pyrene by *Sphingomonas yanoikuyae* JAR02 yielded in 0.2 to 0.3 % $^{14}CO_2$ when grown with plant root exudates (Rentz et al. 2005). Experiments with ^{14}C-labeled pyrene in a sand amended *Mycobacterium* strain KMS and barley plants showed that greater release of $^{14}CO_2$ was observed in the system with barley colonized by KMS than in microcosms containing just the bacterium inoculum or sterile barley plants (Child et al. 2007).

4 Metabolism of ^{14}C-Labeled Organochlorine Pollutants

The organochlorine pollutants are widely distributed and include industrial chemicals, solvents, pesticides, drugs, polychlorinated biphenyls, dioxins, etc. The content of chlorine atoms on the one hand determines the toxicity of these pollutants, and on the other hand defines their resistance to the complete detoxification via oxidative degradation. Therefore, the investigations by using labeled organochlorine pollutants that assess the degree of mineralization of such compounds are very important to evaluate the effectiveness of various tools for remediation technologies.

The main pathway of [^{14}C] 2,4-dichlorophenoxyacetic acid (2,4-D) metabolism in plants is the formation of esters with glucose and malonyl residues (Feung et al. 1976; Sandermann 1987; Viana and Mantell 1998). For example, after penetration of [^{14}C] 2,4-D into the root cells of barley (*Hordeum vulgare*) seedlings the labeled conjugates were detected in the vacuoles and among these conjugates, 80 % was *O*-*β*-D-glycosides of the 2,4-D metabolites (Chkanikov 1985). Other literature data indicates on possibility of formation of some conjugates of 2,4-D metabolites with peptides (Durmishidze et al. 1982; Kakhniashvili 1988; Kakhniashvili et al. 1979). Furthermore, the authors reported that in maize, pea, and kidney bean, along with transformation of the side chain of 2,4-D, aromatic ring degradation takes place. The labeled acyclic organic acids, amino acids, sugars, and CO_2 as products formed from the [1-^{14}C] 2,4-D have been isolated and identified. However, the mineralization degree is low and equals to 1 %.

2,4-D is biodegradable in soils, while adsorption/desorption is influenced by both soil organic matter content and soil pH (Boivin et al. 2005). For example, the greatest mineralization (up to 30 %) of [1–6-^{14}C] 2,4-D occurred in sandy soils containing the least amount of organic carbon (Cycon et al. 2010). Microbial degradation of 2,4-D in soil involves hydroxylation, cleavage of the acid side-chain, decarboxylation, and ring opening (Tomlin 2006). The forming labeled 2,4-dichloroanisole and 2,4-dichlorophenol from ring-labeled [^{14}C] 2,4-D in the soil indicates that hydrolytic cleavage and decarboxylation are potential starting reactions in the transformation of 2,4-D by rhizospheric microorganisms (Smith 1985).

Fungi, especially basidiomycetes, are distinguished by high ability of complete destructin of 2,4-D. Extensive mineralization of ^{14}C-labeled 2,4-D by white rot basidiomycetes *P. chrysosporium* and *Dichomitus squalens* has been demonstrated in liquid media (Reddy et al. 1997; Yadav and Reddy 1992, 1993b). Fungal biotransformation of 2,4-D involve an initial ether cleavage resulting in the formation of 2,4-dichlorophenol and acetate. Further, degradation of chlorophenol intermediate is carried out by ligninolytic peroxidases that catalyze subsequent oxidative dechlorination to a benzoquinone metabolite followed by aromatic ring cleavage and finished by mineralization to $^{14}CO_2$. These microorganisms can degrade polyhalogenated hydrocarbons, which hardly undertake degradation by plants. For instance, as a result of biotransformation of the insecticide lindane (1,2,3,4,5,6-hexachlorocyclohexane) by the white rot fungi *P. chrysosporium*, the polar metabolites such as tetrachlorocyclohexane, tetrachlorocyclohexane epoxide, and tetrachlorocyclohexenol, as well as carbon dioxide are identified (Mougin et al. 1996). Similar metabolites are found among intermediates when lindane undergoes degradation by other fungal strains, e.g., *Trametes hirsutus, Cyathus buller,* and *Phanerochaete sordida* (Singh and Kuhad 1999, 2000). According to these results, hypothetic scheme of lindane mineralization has been proposed (see Fig. 4).

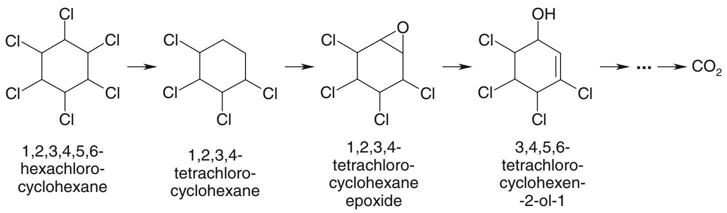


Fig. 4 Hypothetical pathway of lindane degradation by white rot fungi according to Marco-Urrea and Reddy (2012)

The widely used degreasing solvent such as trichloroethylene (TCE) is problematic environmental pollutant due to its chemical stability and toxicity for living organisms. Studies that used [^{14}C] TCE have revealed biological tools for effective removing this pollutant from environment. It has been demonstrated that TCE is mineralized by lignin peroxidase of *P. chrysosporium* cultures grown aerobically (Khindaria et al. 1995). Later research showed that most of using [^{14}C] TCE as the substrate for *P. chrysosporium* undergoes total degradation to $^{14}CO_2$ (Yadav et al. 2000). The plants can significantly enhance TCE mineralization by indigenous microorganisms in soil. It has been shown that plant species bahiagrass (*Paspalum notatum*), Chinese bushclover (*Lespedeza cuneata*), loblolly pine (*Pinus teada*), and goldenrods (*Solidago* sp.) significantly rise degradation level of TCE to carbon dioxide in rhizosphere (Walton and Anderson 1990). The presence of the broad-leaved cattail (*Typha latifolia*) resulted in increased production of labeled CO_2 from 3.2 to 5.3 % in wetland microcosms (Bankston et al. 2002).

Despite the fact that their production is currently prohibited, polichlorinated biphenyls (PCBs) remain to be one of the most problematic pollutants because they hardly undergo degradation. In general, the degree of mineralization of PCBs decreased with an increase in chlorine content. Thus, mineralization of [^{14}C] Aroclor-1242 (42 % chlorine by weight) by *P. chrysosporium* was about 20 %, while that of [^{14}C] Aroclor-1254 (54 % chlorine by weight) ranged from 10 to 14 % (Bumpus and Aust 1987; Eaton 1985; Yadav et al. 1995). Besides strains of *P. chrysosporium,* other fungal cultures are also characterized with capacity to degrade congeners of PCBs containing three and more chlorine atoms in molecule. For instance, *Trametes versicolor*, *Pleurotus ostreatus,* and *Bjerkanderaadusta* mineralize [^{14}C] 2,4,5-trichlorobiphenyl (Beaudette et al. 1998, 2000); *Phlebia brevispora*, as well as *P. chrysosporium* degrades labeled 3,3′,4,4′-tetrchloro-, 2,3′,4,4′,5-pentachloro- and 3,3′,4,4′,5,5′-hexachloro-biphenyls (Kamei et al. 2006).

The metabolism of PCB congeners in plants significantly depends on the plant species, degree of chlorination, and molecular configuration of PCBs (Wilken et al. 2009). In studies with [^{14}C] 2-chlorobiphenyl) in soybean cultures, one dihydroxylated and six different monohydroxylated compounds were detected among conjugates. Hydrolysis of metabolites of [^{14}C] 2,2′,5,5′-tetrachlorobiphenyl in wheat cell cultures yielded four monohydroxylated and three dihydroxylated metabolites.

Polychlorinated dibenzodioxins (PCDDs) are highly toxic and most difficultly degradable environmental pollutants. It has been established that PCDD, similar to PCBs, undergo degradation by several species of white rot fungi (Marco-Urrea and Reddy 2012). For example, *Phlebia lindtneri, Phlebia* sp. MG-60, and an unidentified white rot fungus degraded [^{14}C] 2,7-diCDD to a maximum extent of 6.5 % (Mori and Kondo 2002). *Phlebia* species are able to mineralize tri- and tetra- substituted dioxins, such as 2,3,7-triCDD (18.4–27 %), 1,2,8,9-tetraCDD (11.9–21.1 %), and 1,2,6,7-tetraCDD (14.2–21.5 %) (Kamei et al. 2005).

5 Metabolism of 2,4,6-trinitrotoluene Labeled with ^{14}C in Plants and Microorganisms

Labeled with ^{14}C pollutants were broadly applied for the study of TNT metabolism in plants and microorganisms. For example, the penetration and localization of [1-^{14}C] TNT in soybean plant cells (and maize) was studied via electron microscopic autoradiography. In soybean root cells, [1-^{14}C] TNT was detected as electron-dense label in cell walls, endoplasmic reticulum, mitochondria, plastids, nuclei, nucleolus, and vacuoles (Fig. 5) (Adamia et al. 2006; Kvesitadze et al. 2006); in leaves the label appeared primarily in cell walls, chloroplasts, and vacuoles (Fig. 6) (Adamia et al. 2006).

Attention should be paid to the localization of [1-^{14}C] TNT on membrane structures participating in the transport of reducing equivalents (membranes of the endoplasmic reticulum, mitochondria, and plastids). Supposedly, TNT transformation proceeds in these subcellular organelles.

The results of experiments using [1-^{14}C] TNT for studying the fate of absorbed TNT in soybean seedlings indicate on universal distribution of TNT-labeled carbon atom in low- and high-molecular mass compounds in roots and aboveground parts of plants. The data of these experiments prove ones again the high mobility of TNT and its metabolites in plants (Adamia et al. 2006). Content of labeled TNT and its metabolites among low-molecular compounds in plant roots are much higher than in above ground parts. On the contrary, labeled high-molecular compounds are more intensively in aboveground parts of soybean. It should be proposed that most part (up to 70 %) of metabolites of TNT is conjugated with biopolymers. The physical–chemical analysis of insoluble in 80 % ethanol high-molecular ^{14}C compounds fraction indicates to the existence of two types of TNT metabolites (with amino and carboxyl groups, correlation 4:1), which bind with high-molecular compounds of plants. Apparently, formation of amino and carboxyl groups as a result of TNT transformation by plant enzymes promotes their conjugation with endogenous compounds (Adamia et al. 2006; Khatisashvili et al. 2009). Based on these results and literature data, the hypothetic scheme of TNT metabolism in plants could be presented in Fig. 7.

As is seen from the Fig. 7, the metabolism of TNT in plants proceeds in following way: initially either nitro groups of TNT are reduced to amino groups,

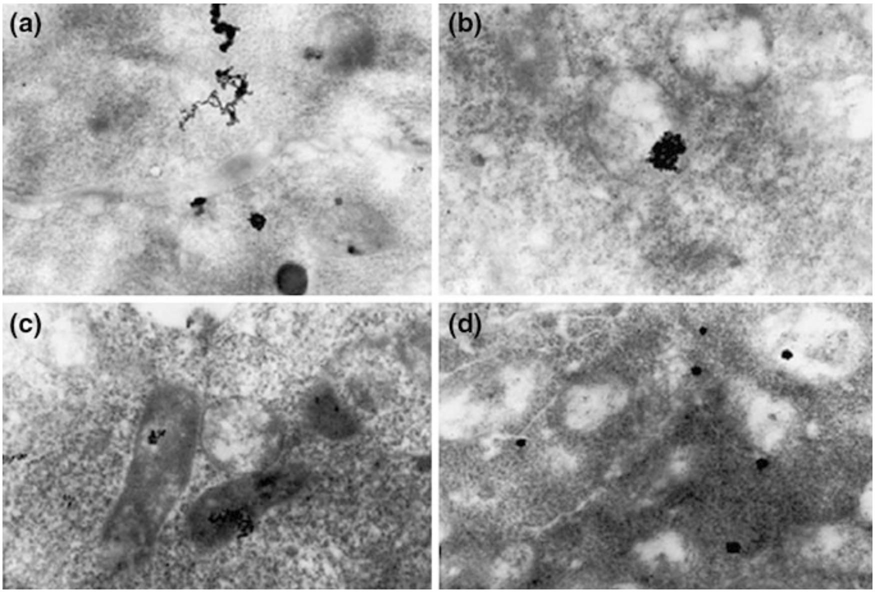


Fig. 5 Cortical cells of roots of soybean seedlings grown in 0.5-mM [1-^{14}C] TNT. **a** Label in mitochondria and on the plasmalemma in the endoplasmic reticulum ×28,000. **b** Label in mitochondria ×48,000. **c** Label in plastids ×36,000. **d** Label in mitochondria and endoplasmic reticulum ×20,000 (Adamia et al. 2006; Kvesitadze et al. 2006)

catalyzed by nitroreductase, or methyl group of the molecule is transformed to carboxyl group, catalyzed by oxidation enzymes (phenoloxidase, preferably). Set of different transferases forming soluble low-molecular (~30 %) and insoluble high-molecular mass conjugates (~70 %) ends the transformation process of TNT. However, the relation between the high molecular conjugates formed in both cases indicates that main part of TNT (80–85 %) is transformed via reduction pathway. Activation of some enzymes of cell basic metabolism, providing the nitroreductase with reduced equivalents of NAD(P)H, suggests their indirect participation in the xenobiotic detoxification (Khatisashvili et al. 2009). Similar works conducted by other authors could be a base for such supposition (Best et al. 1999a, b; Hughes et al. 1997; Schoenmuth and Pestemer 2004; Sens et al. 1998, 1999). After uptake, [1–6-^{14}C] TNT by roots of kidney bean, labeled with ^{14}C conjugates with lignin (20 %), hemicellulose (14 %), and pectin (5 %) are identified (Sens et al. 1998, 1999). Such biopolimers, being widely presented in plant tissues and possessing many free functional groups, actively participate in conjugation with amino groups of intermediates of TNT metabolism. It has been shown that aminodinitrotoluenes (ADNTs), primary products of TNT reduction, conjugate with hemicellulose in the roots of hybrid willow (*Salix* sp.) and Norway spruce (*Picea abies*) trees used in dendroremediation of soils polluted by TNT (Schoenmuth and Pestemer 2004).

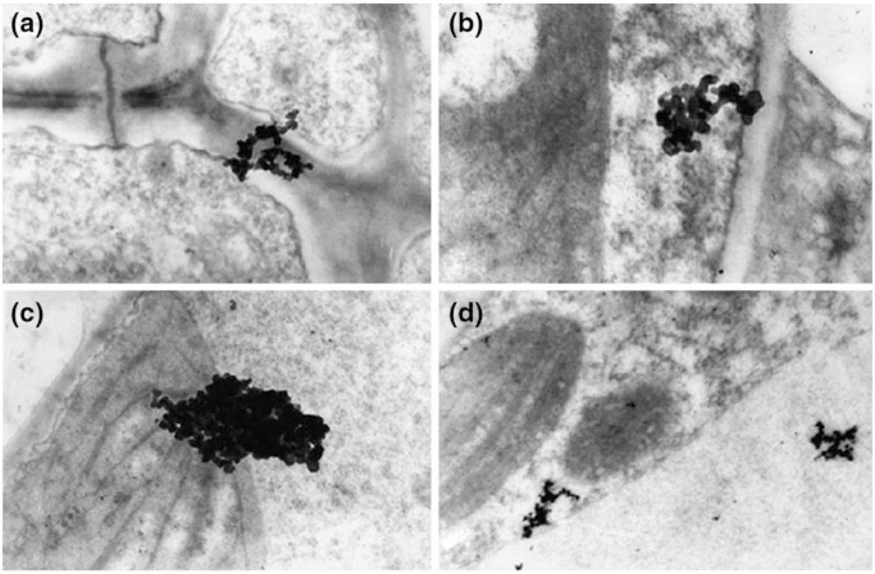


Fig. 6 Cells of leaves of soybean seedlings, grown in 0.5-mM [1-^{14}C] TNT. **a** Label in cell wall and on plasmalemma of the two cells ×64,000. **b** Label on plasmalemma and in periphery cytoplasm ×88,000. **c** Label in a chloroplast ×48,000. **d** Label in vacuole and cytoplasm ×48,000 (Adamia et al. 2006)

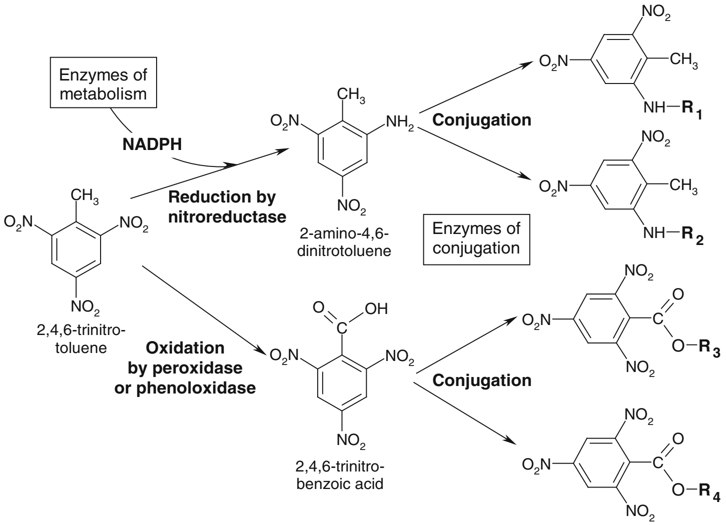


Fig. 7 Supposed pathways of TNT transformation in plants. R_1 and R_3 in scheme are low-molecular mass soluble compounds; R_2 and R_4—high-molecular mass insoluble compounds (Khatisashvili et al. 2009)

Plants ability to uptake and metabolize TNT was confirmed by Hughes et al. (1997). Three plant systems, viz. Madagaskar periwinkle (*Catharanthus roseus*) hairy root cultures, axenic, and native watermilfoil plants (*Myriophyllum* sp.) were exposed to demonstrate reduction of uniformly labeled [^{14}C] TNT, and to evaluate the fates of the labeled carbon atoms. TNT is completely transformed in all plant systems containing viable plant tissue. Aminonitrotoluenes, some unidentified ^{14}C-labeled compounds, extractable plant-associated [^{14}C] fractions that could not be identified as reduction products and bound-residues (plant-associated material that could be quantified after combustion of the plant tissue) are the metabolites that have been found.

Release of $^{14}CO_2$ was not observed in none of the cases of study of [^{14}C]-labeled TNT metabolism in plants. This fact indicates that plants are not able to complete mineralization of this pollutant. Main part of TNT carbon skeleton remains unchanged in plants, however, it is less dangerous to plant cell as it is conjugated with intracellular compounds and deposited in such compartments (cell wall, vacuoles) that are distanced from living important organelles (nucleus, mitochondria, plastids, etc.). Obviously, in such form, conjugates are kept in a cell for a definite period without causing any pathological deviation in cell homeostasis.

First step of transformation of TNT in microorganisms, as well as in plants, is reduction of nitro groups to amino groups. Despite of this similarity, majority of microorganisms more intensively assimilate TNT than plants. It have been shown that microorganisms of different taxonomic groups (bacteria, fungi, yeast) have abilities to assimilate [1-^{14}C] TNT and in all cases the carbon skeleton of TNT undergoes deep biotransformation that is testified by radioactivity of the fractions of organic acids and amino acids (Khatisashvili et al. 2004). Carbon atoms of assimilated and transformed [1–6-^{14}C] TNT are basically used by microorganisms for the biosynthesis of amino acids. In cultivation medium of microscopic fungi, the presence of labeled amino acids is not observed. Among the amino acids, the compounds with aromatic ring (basically phenylalanine and tyrosine) were prevalent, while for organic acids the radioactive label of TNT was mostly detected in fumaric and succinic acids. Fumaric acid is one of the products of biodegradation of the aromatic ring and is easily metabolized into succinic acid. It can be concluded that after reduction of the main part of the assimilated [1–6-^{14}C] TNT molecules, their oxidation follows which leads to removal of the amino groups and cleavage of the aromatic ring, and as a result organic acids are formed as standard cell metabolites. Thus, successive reduction and oxidation reactions complete detoxification of TNT and the atoms of this toxicant become involved in the vital processes of the organism.

Using [^{14}C] TNT, it was shown that microorganisms differently from plants possess the ability of TNT complete mineralization that is proved by the facts of $^{14}CO_2$ release after incubation of certain strains with [1–6-^{14}C] TNT. For example, *Pseudomonas* sp. JLR11 is able to assimilate [1–6-^{14}C] TNT and about 85 % of total TNT was incorporated as cell biomass, and about 1 % of was recovered as $^{14}CO_2$ (Esteve-Núnez and Ramos 1998). The study of biotransformation of labeled TNT by *P. chrysosporium* has shown that in less than 2 weeks, TNT disappeared completely, 11 different labeled metabolites were identified, but mineralization (liberated $^{14}CO_2$) did not exceed 1 %. After 30 days, all of these metabolites disappeared, but mineralization did not exceed 10 % even after the incubation period was increased to 120 days. The biotransformation of TNT was accompanied by the appearance of manganese peroxidase and lignin-dependent peroxidase activities (Hawari et al. 1999).

Application of ^{14}C-labeled TNT contributed to researchers to establish optimum conditions for TNT mineralization. Thus, the cometabolic transformation of 2,4,6-trinitrotoluene (TNT) by an immobilized *P. chrysosporium* culture was investigated under different TNT and/or glycerol feeding conditions. As a result, full mineralization of [1–6-^{14}C] TNT was achieved to a level of 15.3 % following a 41-day incubation period (Rho et al. 2001). Also, it has been shown that the using of surfactant Tween 80 significantly enhanced [1–6-^{14}C] TNT mineralization by *P. chrysosporium,* in particular, 39.0 % of the TNT was respired on day 68 (Hodgson et al. 2001). Radiolabeled [^{14}C] TNT studies revealed 4.14 % mineralization after an incubation period of 163 days by a mixed culture acclimated and maintained on crude oil-containing media (Jason et al. 2004). In other experiments, by using modified Fenton's reagents ($Fe^{2+} + H_2O_2$) and aerobic microorganisms was achieved significant increase in TNT mineralization (Schrader and Hess 2004). These results show promise in the use of combined abiotic-biotic treatment processes for soils contaminated with high concentrations of TNT. From abiotic factors promoting TNT mineralization by *Pseudomonas* strains, pretreatment with alkali should also be mentioned (Herrmann et al. 2007).

6 Conclusion

The reviewed data on studies with application of ^{14}C-labeled xenobiotic allow concluding that plants and microorganisms are capable to degrade wide spectrum of environmental contaminants up to their mineralization, and microorganisms are more potent in this ability.

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^{90}Sr and ^{137}Cs Accumulation in Plants in the Area of Radiation Accidents

N. N. Kazachonok and I. Y. Popova

Abstract An investigation of radioactive contamination of soil, crops, vegetables, feed, grass of hayfields and pastures, wild berries, and mushrooms as a result of radioactive contamination due to operation of radiochemical plant, Production Association (PA) "Mayak," was carried out on the territory of northeastern part of Chelyabinsk region in 2006–2012. ^{90}Sr and ^{137}Cs content in the agricultural products and wild mushrooms in the whole territory of 30–35 km from PA "Mayak" did not exceed maximum permissible level and was not dangerous for the population. ^{90}Sr accumulation in wild berries and grass of hayfield and pastures on the territory of East-Ural radioactive trace did not exceed the radiological sanitary limits which could be dangerous for the population and farm animals. On the rest of the territory, both berries and grass were non-contaminated. The accumulation coefficients of ^{90}Sr and ^{137}Cs in agricultural products and wild plants and mushrooms vary significantly. The highest values of the accumulation coefficients, sometimes >1, were found for grass of hayfields and pastures. Among agricultural plants, the highest values of the accumulation coefficients were found for carrot, Sudan grass, and corn, whereas the lowest values were found for cabbage, beetroot, and potato. The accumulation coefficients of the radionuclides found for vegetables from private farmers were lower than the ones from large agricultural plant. A content of ^{90}Sr and ^{137}Cs in soil in an easy accessible form for the plants depends on the soil humidity and may vary significantly. ^{90}Sr deposited in soil is transferred into soil solution as ionic species. ^{137}Cs in soil solution is present as colloidal species.

Keywords Radioactive contamination · East-Ural radioactive trace · Strontium-90 · Cesium-137 · Soil · Grass · Vegetables · Agricultural goods · Accumulation coefficient

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Contents

1 Introduction

The forecasting of entry of radioactive isotopes into the products of agriculture and forestry in the areas affected by radioactive contamination is an important and urgent problem. Despite increased security measures at nuclear power plants and radiochemical enterprises, radiation accidents accompanied by the release of radioactive substances into the environment are regularly happening on the planet. The study of radionuclides entry into the plants in 50–60 years after the fallout of radioactive substances on the soil surface is necessary for a long-term forecasting of radiation risks for people and the environment.

2 Materials and Methods

The researches have been conducted in 2006–2012 in the territory of northeastern part of Chelyabinsk region that suffered from radioactive contamination caused by the activity of radiochemical industrial complex of the Production Association "Mayak." The specific activity of ^{137}Cs in the soil samples was measured by means of scintillation gamma-ray spectrometer with the software "Progress." From 2011, the spectrometer facility MKC-01A "MULTIRAD" was used for this purpose. In the low-activity soil samples and in the plant ash, ^{137}Cs level was measured using the radiochemical iodine–antimony method after concentrating it on the nickel ferrocyanide. The specific activity of ^{90}Sr in the samples was measured by means of the extractive method based on daughter ^{90}Y using monoisooctylmethylphosphonate. The ß-activity of the selected radionuclides was measured using low-background radiometric facilities UMF-1500 and UMF-2000 with flame-photometric control of strontium carrier yield. All applied methods and measuring means have state calibration certificates.

3 Results and Discussion

Accumulation of ^{90}Sr and ^{137}Cs in the cereal crops and vegetable harvests under the conditions of a large agricultural enterprise. The ability of plants to accumulate radioactive substances is shown by the proportionality coefficients (C_p) between the soil contamination level and the level of contamination of agricultures. Also used are the transport coefficient (C_t)—the ratio of the radionuclide-specific activity in the marketable part of the harvest to the soil contamination density—and the accumulation coefficient (C_a)—the ratio of the radionuclide-specific activity in the marketable part of the harvest to the specific activity of the radionuclide in soil. These coefficients and their dependence on various factors are studied by many researchers.

We conducted research in 2007 in the territory of the agricultural enterprise «Sovkhoz Beregovoy» LLC. The territory of this enterprise was situated in the middle part of the East-Ural radioactive trace (EURT) that resulted from the explosion of a waste tank of the Production Association "Mayak" in 1957. The nearest settlements are Beregovoy, Karabolka, and Bulzi. The soil on which the "Sovkhoz Beregovoy" LLC is situated was formed as a gray forest medium to heavy loamy soil. The soil was treated for many years, its agrochemical properties have changed, and the humus horizon was exhausted in some places. Nevertheless, at that stage of the study when calculating the contamination density, we viewed it as a gray forest heavy loamy soil.

In all sampling points, the density of contamination with ^{137}Cs and ^{90}Sr exceeds the level determined by global fallouts. The average density of contamination with ^{137}Cs of a 0- to 40-cm soil layer from eastern irrigated field with vegetable rotation is 6.3 ± 1.1 kBq^{-1} m^2 and with ^{90}Sr is 8.1 ± 1.5 kBq^{-1} m^2. The contamination with ^{90}Sr of a 0–40 cm soil layer from the southern part of the farm is 7.4 ± 1.8 k Bq^{-1} m^2, and the contamination of a 0–20 cm soil layer with ^{137}Cs is 4.4 ± 1.8 kBq^{-1} m^2. The contamination of a 0–40 cm soil layer from the northern part with ^{137}Cs is 10.4 ± 1.8 kBq^{-1} m^2 and with ^{90}Sr is 45.9 ± 14.1 kBq^{-1} m^2. The highest contamination with ^{90}Sr (111.5 ± 28.9 kBq^{-1} m^2) is observed between 6 and 10 km from the Beregovoy village, where goes the axis of EURT.

The specific activity of samples of agricultural products fluctuated widely. The least contaminated were cabbage, beets, and potatoes. And the specific activity of ^{90}Sr and ^{137}Cs did not exceed 1 Bq kg^{-1}. The maximum permissible level of ^{137}Cs in vegetables is 120 Bq kg^{-1} and ^{90}Sr is 40 Bq kg^{-1} (SanPiN2.2.2.1078-01). This is due to a small contamination of soil in the eastern part and low values of C_a. The accumulation coefficients are shown in the Table 1. C_a of cereal crops is a little higher; in addition, some samples were taken in areas with a high contamination density. Therefore, the specific activity of ^{37}Cs in grain ranged from 0.05 to 3.42 Bq kg^{-1} and that of ^{90}Sr ranged from 0.45 to 28.1 Bq kg^{-1}. The maximum permissible level of ^{137}Cs in the food grain is 70 Bq kg^{-1}, and the maximum permissible level of ^{90}Sr in the food grain is 40 Bq kg^{-1} (SanPiN2.2.2.1078-01). The greatest values of C_a were observed in carrots, Sudan grass, and corn.

Table 1 Average values of C_a ^{137}Cs and ^{90}Sr in commodity part of crops for a layer of 0–20 cm of the gray forest soil

Culture	Production	Grade	C_a	
			^{137}Cs	^{90}Sr
Peas	Grain	Agrointel	0.062 ± 0.035	0.084 ± 0.029
Wheat	Grain	Duet	0.078 ± 0.052	0.036 ± 0.011
Oats	Grain	Orion	0.032 ± 0.016	0.054 ± 0.025
Barley	Grain	Omsk-90	0.039 ± 0.032	0.070 ± 0.050
Onions	–	–	0.016 ± 0.008	0.026 ± 0.009
Cabbage	Head of cabbage	Surprise	0.019 ± 0.008	0.029 ± 0.005
Carrots	Root crop	Samson	0.146 ± 0.187	0.237 ± 0.251
Beet	Root crop	Boro	0.016 ± 0.008	0.026 ± 0.007
Potatoes	Tubers	Nevsky	0.008 ± 0.003	0.020 ± 0.012
Corn	Grass	Ekaterina	0.049 ± 0.040	0.242 ± 0.186
Sudan grass	Grass	Kamyshlovskaya	0.083 ± 0.035	0.175 ± 0.054

However, these cultures were not grown on the most contaminated territories in the year when the study was conducted, so their specific activity did not exceed the maximum permissible level and ranged in carrots from 0.18 to 4.86 Bq kg^{-1} for ^{137}Cs and from 0.4 to 5.77 Bq kg^{-1} for ^{90}Sr, and in silage cultures from 0.54 to 3.2 Bq kg^{-1} for ^{137}Cs and from 1.2 to 21.8 Bq kg^{-1} for ^{90}Sr. Although in the year when the study was conducted, the permissible levels of radionuclides were not exceeded, we cannot say with certainty that contamination could not be greater in other weather conditions. Therefore, it required an annual radiological control of products grown in the territory of the northern part and in the area of the middle part of the road Bulzi–Beregovoy.

It is considered that as far as radionuclides change into bound forms that are less available to plants, their C_p decrease on the average. Thus, during the first year after the formation of EURT, C_t for potatoes (in Bq kg^{-1}/37 kBq^{-1} m^2) was 6.7 (according to our calculations, this corresponds approximately to C_a—0.044). In 1961–1962, C_t for grain was 9.3 (corresponds to C_a—0.060), for potatoes—6.7 (corresponds to C_a—0.044), for cabbage—11 (corresponds to C_a—0.071), for carrots—7.4 (corresponds to C_a—0.048), and for onions—8.4 (corresponds to C_a—0.054). During 1965–1967, according to different authors, C_t for grain was 6.7 (corresponds to C_a—0.044), for potatoes—0.6 (corresponds to C_a—0.004) and 1.0 (corresponds to C_a—0.006), for cabbage—8.9 (corresponds to C_a—0.058), for onions—15 (corresponds to C_a—0.097), and for carrots—17.4 (corresponds to C_a—0.113). In 1997, C_t for potatoes were 1.5 (corresponds to C_a—0.010) EMCRA (2001).

In 1999, in the Guidelines for agro-industry and forestry in the sanitary protection zone of the East-Ural radioactive trace were given summaries of the planned accumulation of ^{90}Sr in products that correspond according to our calculations in gray forest soils to the following C_a: wheat—0.038, barley—0.029, oats—0.036, corn (herbage)—0.408, potatoes—0.04, beets—0.062, and cabbage—0.060 (The guide to conducting agro-industrial production and forestry in the territory of a sanitary protection zone East Ural radioactive trace/Chelyabinsk: Administrator. Chernobyl Region 1999).

As can be seen from Table 1, the values of C_a for oats and barley that we obtained in 2007 were higher than values according to the summary data of 1999; for other cultures, they were lower. However, it must be considered that the assortment of agricultures is constantly changing and that even for the same cultivar in the same field at different sampling points, C_a and C_t can vary greatly.

Species and cultivars of agricultural plants vary in their ability to absorb ions selectively. Studies show that varietal differences in the accumulation of ^{137}Cs between the cultivars of cereal crops and pulses reach three times (Malikov et al. 1981). In the study of the ability to accumulate ^{90}Sr of 54 wheat cultivars, the intervarietal differences in two years amounted to 2.9 and 3.9 times (Korneeva et al. 1976). Four years after the Chernobyl accident were published the data that, when the cultivars of cereals were properly selected, the amount of ^{137}Cs in the harvest from the contaminated soils decreased by two to six times and in potatoes, by 13 times (Aleksakhin et al. 1990), whereas C_t are not the same on different soil types, so in 1965–1967, they ranged for grain (in Bq kg^{-1}/37 kBq^{-1} m^{-2}) from 7.4 (on leached black earth) to 13 on the gray forest soil and 18.5 on the soddy-podzolic soil (EMCRA 2001).

The availability of radionuclides to plants is influenced by their distribution in the soil profile and the agrochemical soil properties. In 1986–1990, in the territory of Russia after the Chernobyl accident were taken protective measures in order to reduce the content of ^{137}Cs in plant products (liming of acid soils, use of higher doses of phosphorus–potassium fertilizers). As a result, the contamination of grain and potatoes decreased by 1990 by 20–30 times. [The atlas of modern and expected aspects of consequences of the Chernobyl accident in affected territories of Russia and Belarus (ASPA Russia-Belarus, Moscow-Minsk 2009)].

This diversity is especially expressed in the samples in which specific activity is comparable with the level of sensitivity of the method of radiochemical analysis. Therefore, we cannot say with certainty that in the territory of EURT, C_p continue to decrease in the remote period after the accident.

3.1 Accumulation of ^{90}Sr and ^{137}Cs in the Harvest of Vegetables from Private Farms

In the private farms, the conditions of entry of radionuclides into plants vary significantly. The farmers usually do not follow the rules of agricultural machinery, use manual labor, and bring into the soil a small amount of mineral fertilizers. As an organic fertilizer, the farmers use manure from animals fed with contaminated feed. In addition in the farms are not usually grown purebred and revitalized plants. Therefore, the content of radionuclides in vegetables from private farms may be different than the content of radionuclides in vegetables from large agricultural enterprises.

For example, in the Bryansk region, after the Chernobyl accident, as a rule, the levels of contamination of products produced on private farms is 1.5–2.0 times higher than in the collective farms. [The atlas of modern and expected aspects of consequences of the Chernobyl accident in affected territories of Russia and Belarus (ASPA Russia-Belarus, Moscow-Minsk 2009).]

For assessing the contamination of settlements in the zone of influence of PA "Mayak" in 2009–2011 were taken samples of garden soil, potatoes, and other vegetables.

During the study period, 83 samples of garden soil were taken. Table 2 presents the average values of specific activity of radionuclides in the soil from different settlements. There is a significant inverse correlation of the average specific activity of ^{137}Cs in the soil of 36 settlements with distance from the source of contamination—$r = -0.43$ ($p < 0.01$). For the activity of ^{90}Sr, the correlation with the distance is not statistically significant and positive $r = 0.29$. This is due to the fact that the most contaminated with ^{90}Sr is the soil in the settlements that are close to the territory of EURT—Karabolka and Allaki and located at a distance of 38–39 km from the source of contamination. The highest coefficient of inverse correlation was obtained between the activity of ^{137}Cs in the soil and the angle of deviation from the southeast direction (azimuth 136°), $r = -0.49$ ($p < 0.01$). For ^{90}Sr, the direction for which the strongest connection was detected corresponds to the direction of axis of EURT (azimuth 30°), $r = -0.34$ ($p < 0.05$).

It should be noted that the levels of soil contamination with radionuclides within one settlement can vary greatly. Apparently, this is connected with a multi-year application of manure produced by cows fed with contaminated hay. So, in the settlement Karabolka on the household plot under the address Shkolnaya Street, 20, the activity of ^{90}Sr in the hay was 56.1 Bq kg^{-1} and in the soil, it was 279 Bq kg^{-1}. On a plot under the address Shkolnaya Street, 11-1, the activity of ^{90}Sr in a sample of hay taken in April 2011 was 2,524 Bq kg^{-1} and in the sample taken in June 2011, it was 1,709 Bq kg^{-1}. In five soil samples taken from this plot using the envelope method, the activity of ^{90}Sr varied from 239 to 820 Bq kg^{-1}. On the neighboring plot under the address Shkolnaya Street, 26, located across the road, are no cows at the moment. The activity of ^{90}Sr in the soil is here 134 Bq kg^{-1}.

We can conclude from the results of tests conducted by Urals Research Center for Radiation Medicine earlier that usually about 10 % of the samples of garden soil, potatoes, vegetables, and other products produced in the personal household plots in the studied area are very different in content of radionuclides. The reason for this is that some owners violate the regime of EURT protection zone.

Therefore, for a rough estimation of the radiation situation in the whole territory, we calculated the average values for 90 % of the samples with the lowest values of radionuclide activity.

The average activity of ^{137}Cs in 90 % of the soil samples was 58 Bq kg^{-1}, and the maximum activity was 193 Bq kg^{-1} (in the settlement Kyzylbulyak). The

Table 2 Specific activity and C_a ^{137}Cs and ^{90}Sr in the soil and potatoes on the average on settlements in 2009–2011

Settlement	Soil Bq kg^{-1}		Potatoes Bq kg^{-1}		C_a	
	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr
Allaki	38.1	198.9	0.36	0.78	0.0094	0.0039
Argayash	47	24.2	0.39	0.2	0.0083	0.0083
Ayazgulova	103.7	40.6	0.52	0.33	0.0050	0.0081
Bizhelyak	111	66	0.97	0.96	0.0087	0.0145
Bolshoe Taskino	98.2	46.8	0.64	0.28	0.0065	0.0060
Bolshoi Kuyash	124	43.3	0.53	0.58	0.0043	0.0134
Gornii	83	24.6	0.41	0.35	0.0049	0.0142
Ibragimova	61	35.7	0.59	0.38	0.0097	0.0106
Karabolka	34.6	423.4	0.64	1.11	0.0185	0.0026
Karagaykul	46.3	43.7	1.33	0.3	0.0287	0.0069
Kasli	32.8	99.8	0.46	0.38	0.0140	0.0038
Komsomolskii	38.5	36.5	0.28	0.12	0.0073	0.0033
Krasnii Partisan	42	76.2	0.37	0.51	0.0088	0.0067
Kuvalzhikha	42.7	23.3	0.25	0.29	0.0059	0.0124
Kuvalzhikha	29	4.9	0.31	–	0.0107	–
Kuznechikha	31.4	26.8	0.68	0.09	0.0217	0.0034
Kurmanova	27.5	20.4	0.19	0.12	0.0069	0.0059
Kyzylbulyak	193	136.9	0.44	0.91	0.0023	0.0066
Kyshtym	36	28.8	0.87	0.22	0.0242	0.0076
Malii Kunashak	75	77.5	0.90	0.44	0.0120	0.0057
Mauk	26	29.2	0.36	0.24	0.0138	0.0082
Novogornii	90	48.6	0.69	0.63	0.0077	0.0130
Novaya Soboleva	33.8	19	0.26	0.15	0.0077	0.0079
Sarykulmyak	109.3	70.7	0.29	0.52	0.0027	0.0074
Severnii	25.4	36.6	0.84	0.28	0.0331	0.0077
Selezni	158.5	86.4	0.55	0.21	0.0035	0.0024
Slyudorudnik	29.6	36.5	0.47	0.22	0.0159	0.0060
Suleymanova	159.7	74.5	0.59	0.39	0.0037	0.0052
Syrgaydi	39	24	0.41	0.14	0.0105	0.0058
Tayginka	57.9	57.4	1.11	0.67	0.0192	0.0117
Tatysh	131	71.2	0.79	0.82	0.0060	0.0115
Tyubuk	18.2	63.2	0.26	0.39	0.0143	0.0062
Uvildi	33.2	29.4	1.00	0.35	0.0301	0.0119
Hudayberdinsky	147.2	92.1	0.58	0.38	0.0039	0.0041

average activity of ^{90}Sr was 44.4 Bq kg^{-1}; the maximum activity of ^{90}Sr was 820 Bq kg^{-1} (in the settlement Karabolka).

During the study period were selected 95 samples of potatoes. The average activity of ^{137}Cs in 90 % of the samples was 0.44 Bq kg^{-1}, and the maximum activity was 2.43 Bq kg^{-1}. The average activity of ^{90}Sr in 90 % of samples was 0.34 Bq kg^{-1}, and the maximum activity was 4.12 Bq kg^{-1}. In all samples of potatoes, the content of ^{137}Cs and ^{90}Sr is significantly lower than the maximum

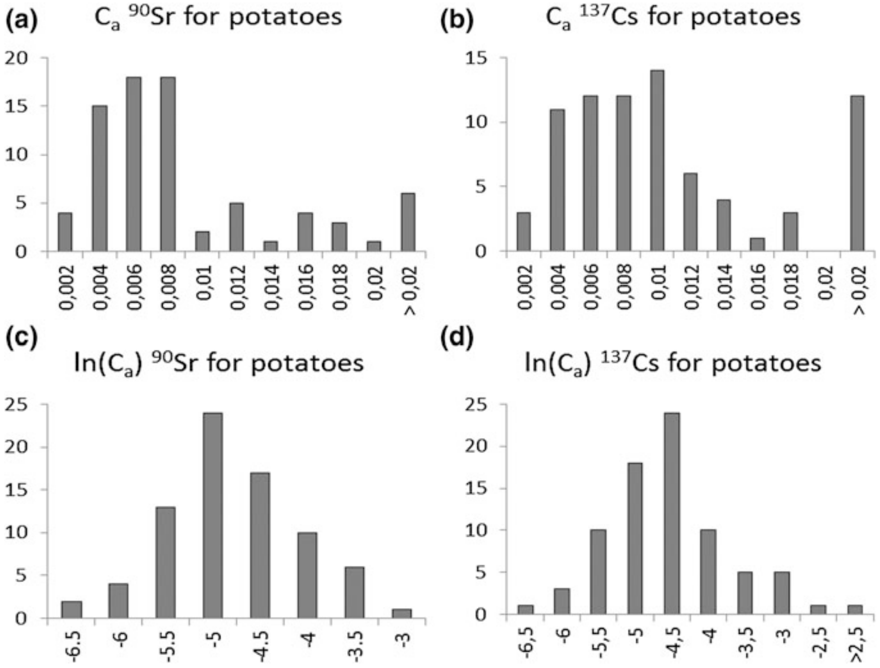

Fig. 1 **a** The histogram of distribution of C_a ^{90}Sr for potatoes. **b** The histogram of distribution of C_a ^{137}Cs for potatoes. **c** The histogram of distribution of ln(C_a) ^{90}Sr for potatoes. **d** The histogram of distribution of ln(C_a) ^{137}Cs for potatoes

permissible levels (in potatoes and vegetables, MPL of ^{137}Cs is 80 Bq kg^{-1} and MPL of ^{90}Sr is 40 Bq kg^{-1}, SanPiN 2.3.2.1078-01). Specific activities of ^{137}Cs and ^{90}Sr in potatoes are not connected—$r = -0.04$.

For all pairs of samples "soil—potatoes" were calculated accumulation for coefficients. The ability of potatoes to accumulate ^{137}Cs from soil (C_a) does not correlate with the ability to accumulate ^{90}Sr—$r = -0.009$.

The ranges of fluctuations of C_a ^{90}Sr and C_a ^{137}Cs are very large. Figure 1a, b shows histograms of distribution of radionuclides C_a in potatoes.

The histograms illustrate that the values of C_a of ^{90}Sr and ^{137}Cs in potatoes from different household plots in the zone of influence of PA "Mayak" can vary considerably. Furthermore, the distribution of C_a is not normal. As can be seen from the Fig. 1c and d, the lognormal distribution suits better for statistical processing of data about C_a. However, as mentioned above, the violation of the protection zone regime by some owners complicates the statistical analysis. In our opinion, the most promising in this case is the application of the principles of fuzzy logic (Kazachonok 2013), but a correct development of the analysis method requires a large amount of experimental data.

Table 2 presents the average values of specific activity of radionuclides in potatoes from different settlements and the values of their C_a.

As can be seen from Table 2, C_a ^{137}Cs in potatoes in private farms were similar to C_a ^{137}Cs in «Sovkhoz Beregovoy» LLC. C_a ^{90}Sr in private farms appeared to be several times lower. As exactly ^{90}Sr poses the greatest danger in the territory of EURT, this difference requires further study.

We also analyzed 14 samples of carrots and 12 samples of beets. The average specific activity of ^{137}Cs in 90 % of the carrots samples was 0.59 Bq kg^{-1}, and the maximum activity of ^{137}Cs in carrots was 3.9 Bq kg^{-1}. The average specific activity of ^{137}Cs in 90 % of the beets samples was 0.35 Bq kg^{-1}, and the maximum activity of ^{137}Cs in the beets was 1.57 Bq kg^{-1}. For ^{90}Sr, the average activity was, respectively, 1.41 Bq kg^{-1} in carrots and 1.31 Bq kg^{-1} in beets, the maximum values of ^{90}Sr activity were 3.98 Bq kg^{-1} in carrots and 19.6 Bq kg^{-1} in beets. We have analyzed one sample of cabbage, one sample of radish and one sample of apples. The activity of ^{90}Sr and ^{137}Cs did not exceed their 1.0 Bq kg^{-1}.

Radionuclides C_a vary greatly. This complicates very much the prediction of radioactive contamination of agricultural products. In addition, radionuclides C_a in vegetables in farms were lower than in «Sovkhoz Beregovoy» LLC.

3.2 *Accumulation of ^{90}Sr and ^{137}Cs in Grass Biomass in Natural Ecosystems*

The study of regularities of radionuclides accumulation in the grass biomass is necessary for predicting the radioactive contamination of feed for farm animals.

In 2009–2011, we took 50 samples of hay from private farms. The average specific activity of ^{137}Cs in the hay in 90 % of the samples was 8.9 Bq kg^{-1}, and the maximum specific activity was 70.4 Bq kg^{-1} (in the village of Bolshoe Taskino). The average specific activity of ^{90}Sr in 90 % of samples was 23 Bq kg^{-1}, and the maximum values that exceed the reference level had the hay samples from the village of Allaki (112, 656 and 1,132 Bq kg^{-1}) and from the village of Karabolka (1,709 Bq kg^{-1} and 2,524 Bq kg^{-1}). The owners of household plots knew that they make hay on the axis of EURT and were aware that it is forbidden to make hay in these plots. The activities of ^{137}Cs and ^{90}Sr in hay do not correlate, $r = -0.07$. Therefore, a study of radionuclide accumulation in herbaceous plants is important.

In 2008–2011, we measured the content of ^{90}Sr and ^{137}Cs in the aboveground biomass of herbaceous plants from the grasslands on the territory within a radius of 30–35 km from the PA “Mayak.”

The farmers in the Chelyabinsk region make hay and graze cows on natural grasslands. Therefore, we did not classify the samples by the species of plant, but collected and analyzed the entire biomass of grass at a distance of not more than 1 m from the soil sampling point. All values of radionuclides content in the grass and C_a are calculated for the dry weight of grass. The reference levels (RL) of radionuclides in the feed according to the “instructions on the radiological control

Table 3 RL of radionuclides in a stern Bq kg^{-1}

Type of a forage	^{90}Sr	^{137}Cs
Hay	100	600
Fresh grass	50	370

Table 4 The contents ^{90}Sr and ^{137}Cs in a grass on a haying site on the first transect

Place of selection of test	Specific activity Bq kg^{-1}		C_a		C_t	
	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
1	366	17.9	0.25	0.048	1.10	0.193
2	677	6.1	0.48	0.024	2.03	0.104
3	584	12.4	0.71	0.057	3.31	0.248
4	483	6.8	0.37	0.024	1.38	0.093
5	361	11.4	0.46	0.076	2.12	0.333
6	1,454	31.8	2.10	0.142	9.67	0.629
7	985	17.7	1.08	0.083	4.78	0.373
8	876	14.5	1.15	0.080	4.68	0.356
9	535	16.0	0.59	0.061	2.65	0.276
10	549	50	0.88	0.221	3.40	0.844
11	210	28.3	0.51	0.118	2.21	0.520
Average value			0.78 ± 0.31	0.08 ± 0.03	3.4 ± 1.4	0.36 ± 0.13

of feed quality" (The instruction about radiological quality control of forages. RL of the content of radionuclides of caesium-134, -137 and strontium-90 in sterns and feed additives)/(it is approved by the Ministry of Agriculture of the Russian Federation 01.12.1994 N 13-7-2/216)) are presented in Table 3.

In 2008, we measured the content of ^{90}Sr and ^{137}Cs in grass in two transects that cross EURT perpendicular (Tables 4 and 5). The first transect was located 20 km away from the PA "Mayak" in the grassland at the top of a slight slope to the shore of Lake Alabuga (Table 4). The first soil and grass sampling point was located at a distance of 20 m from the skirt of the birch forest, and the subsequent points were separated by a distance of 20 m from the previous points. Point 11 was at a distance of 40 m from the shore of Lake Alabuga.

During the study period, the density of soil contamination with ^{90}Sr in this area ranged from 161 to 350 kBq^{-1} m^2 and the specific activity of ^{90}Sr in grass samples in all sampling points was many times higher than RL. The values of C_a ^{90}Sr in grass are high, in some cases they exceed 1.0. Despite the fact that all sampling points were located within an ecosystem that has homogeneous species composition, the range of C_a values is quite large.

The grass contamination with ^{137}Cs in this area did not exceed RL, and C_a ^{137}Cs is significantly lower than C_a ^{90}Sr. The connection between C_a ^{90}Sr and C_a ^{137}Cs was not found, the correlation coefficient—0.50. The correlation between the

Table 5 The contents ^{90}Sr and ^{137}Cs in a grass on the second transect

Ecosystem	Place of selection of test (distance from Chelyabinsk in km)	Specific activity Bq kg^{-1}		C_a		C_t	
		^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
Meadow	94	48.9	7.30	2.27	0.181	17.21	1.499
Wood	95	120[a]	6.60	1.94	0.068	11.15	0.539
Field	96	700[a]	47.10	3.79	2.639	30.86	21.619
Field	97	169[a]	10.60	0.64	0.101	5.30	0.845
Field	98	1400[a]	10.10	3.06	0.124	25.03	1.032
Field	98.5	640[a]	11.70	2.50	0.111	13.40	0.843
Field	99	88.6	7.80	0.74	0.152	6.19	1.265
Wood	100	58.8	6.50	0.71	0.025	5.27	0.204
Meadow	101	23.9	62.60	1.38	0.824	10.79	6.815
Wood	102	50.6	30.60	0.66	0.132	5.41	1.085
Field	103	181[a]	6.50	7.07	0.176	55.52	1.462
Wood	104	28.7	14.10	0.90	0.034	4.72	0.278
Average value				2.1 ± 1.0	0.38 ± 0.42	15.9 ± 8.5	3.1 ± 3.4

Note [a] above a reference level

specific activity of ^{90}Sr and ^{137}Cs in grass is even lower—0.15. The dependence of C_a and C_t on the average activity of ^{90}Sr and ^{137}Cs in soil and on soil contamination density with ^{90}Sr and ^{137}Cs was not detected.

The second transect was located 30 km away from the PA “Mayak.” The soil and grass sampling points were marked according to the distance from Chelyabinsk city. Table 5 presents data on the content of ^{90}Sr and ^{137}Cs in the grass on this transect. In this area, the sampling points were located in different ecosystems: birch forest, pine forest, grassland, hayfield, and neglected field. In six grass samples of 12, the activity of ^{90}Sr exceeded 100 Bq kg^{-1}, and at one point, it amounted to 1,400 Bq kg^{-1}. The values of C_a are very high too, especially in meadows and fields. The spread of C_a values is also very large; especially large is the spread of C_a ^{137}Cs. We assume that this can be explained by the fact that sampling was performed at the end of the growing season, when the accumulation of mineral elements in plant biomass is maximal. In winter, overwintering plants and perennials, the potassium content in the cytoplasm increases while preparation for the winter. Parallel can be accumulated its biochemical analogue—^{137}Cs.

In 2009–2012 was studied the contamination of grass in the territory within a radius of 30–35 km from PA “Mayak.” Grass on the entire territory of study contained a relatively small amount of ^{137}Cs. Even in the EURT, the maximum activity of ^{137}Cs was 62.6 Bq kg^{-1}, and out of EURT, it was from 2.5 to 14.1 Bq kg^{-1}. C_a ^{137}Cs during the study period was 0.06–0.08, so we can assume that the excess of RL of ^{137}Cs accumulation in grass in the areas of settlements is hardly probable. The accumulation of ^{90}Sr in the grass outside the EURT area is also small—from 6.9 to 31.5 Bq kg^{-1}. However, C_a ^{90}Sr is significantly higher than C_a ^{137}Cs, and on the

Table 6 C_t technogenic and natural radionuclides concerning a layer of earth of 0–40 cm (Bq kg^{-1}) (kBq^{-1} sq. m^{-1})

Distance from water in M	^{137}Cs	^{90}Sr	^{40}K	^{226}Ra	^{232}Th
10	0.8	3.5	7.1	In the soil it is not found	In the soil it is not found
10	1.0	4.4	6.6	6.3	In a grass it is not found
20	0.7	7.3	5.0	11.3	In a grass it is not found
50	0.2	0.6	3.7	1.8	0.9
50	0.1	2.3	3.2	3.7	In a grass it is not found

average, in different years of study, it was 0.55–0.78, and in some samples, it exceeded 1.0. The accumulation of ^{90}Sr increases apparently at the end of vegetation to a greater extent than the accumulation of ^{137}Cs. Grass selected on July 15, 2011 near the village of Bolshoy Kuyash contained 3.1 Bq kg^{-1} of ^{137}Cs and 13.5 Bq kg^{-1} of ^{90}Sr. Grass selected in the same point on September 27, 2011 contained 4.7 Bq kg^{-1} of ^{137}Cs and 30.9 Bq kg^{-1} of ^{90}Sr. In September 2008, the coefficient of accumulation of ^{90}Sr in the grass averaged 2.14.

In the areas of settlements located near the axis of EURT (Karabolka, Allaki, Bolshoy Kuyash), the specific activity of ^{90}Sr in the grass can exceed RL. Next to the Lake Alabuga located near the axis of EURT in all grass samples, the content of ^{90}Sr exceeded by several times the reference level and reached 2,630 Bq kg^{-1} in 2011.

The study of radionuclides accumulation in the grass from Techa River floodplain was complicated by the fact that the distribution of ^{90}Sr and ^{137}Cs in the profile of the floodplain soil is very heterogeneous. In the meadow floodplain soils, the major part of radionuclides remains in the upper soil layer and therefore, C_a ^{90}Sr and ^{137}Cs can be calculated based on the average content of these radionuclides in the upper soil layer. The calculation of C_t for these soils is also easy. Table 6 shows the values of C_t of anthropogenic and natural radionuclides in grass samples taken from the pasture on the bank of Techa River near the village of Zatechenskoe. When comparing the data in Tables 4, 5, and 6, it can be seen that C_t ^{90}Sr and ^{137}Cs in floodplain meadow soil and meadow soil near the Lake Alabuga differ only a little.

While calculating C_a in bog soils, the following factors must be considered:

1. Plant roots are short on air and have too much water, so they are situated in the upper soil layer.
2. The greatest content of radionuclides may be in the deep layers of the soil.
3. The highest concentration of water-soluble forms of radionuclides may be in the upper soil layer due to capillary rise and evaporation of soil water.
4. Floodplain soil is composed of a very large number of heterogeneous layers, so it is very difficult to measure the floodplain soil bulk density and to calculate the contamination density.

Table 7 shows the results of the analysis of floodplain grass and soil samples taken on the right bank of the River Techa near the bog Asanovoe at 5 m from the

Table 7 The contents ^{90}Sr and ^{137}Cs in the inundated soil and a grass in 2012 on the Asanovy bog, Bq kg^{-1}

Selection depth in m^2	Test	^{90}Sr	^{137}Cs
	Grass	1,380	4,673
	Peat	4,180	309,000
0–10	Soil	5,989	565,000
10–20	Soil	6,584	649,00
20–30	Soil	6,227	249,000
30–40	Soil	9,097	28,600
40–50	Soil	8,273	20,400
50–60	Soil	7,759	5,388
60–70	Soil	6,405	2,050
70–80	Soil	1,763	844
80–90	Soil	827	619
90–100	Soil	466	433

water. It is impossible to choose correctly the soil layer for calculation of C_a. It is necessary for calculation of C_a to measure accurately the bulk density of the soil and the activity of radionuclide in each thin layer. Bog soil is always waterlogged, so it is very difficult to divide it into layers.

3.3 Accumulation of ^{90}Sr and ^{137}Cs in Forest Products

In 2008–2011, we measured the content of ^{90}Sr and ^{137}Cs in wood, berries, and mushrooms.

Table 8 shows the values of the specific activity of ^{90}Sr and ^{137}Cs in young birch before the leaves start to yellow and fall off. The samples were taken on the axis of EURT 30 km away from the PA “Mayak” and 99 km away from Chelyabinsk. ^{90}Sr is mostly accumulated in the leaves, and ^{137}Cs is mostly accumulated in the branches. In general, C_a of radionuclides in birch and grass sampled at the same place (Table 5) differ only a little.

On October 31, 2008, we collected the fallen leaves in the birch forest near the Lake Alabuga. The specific activity of ^{90}Sr in fallen leaves was 5,904 Bq kg^{-1}, and that of ^{137}Cs was 54 Bq kg^{-1}. The annual contribution of yearly litter to the pollution of forest floor with ^{90}Sr is there estimated at 2.37 kBq^{-1} m^2 or 2.1 % of the floor contamination that existed in the spring 2008. The contribution of litter to the contamination of floor with ^{137}Cs was 0.02 kBq^{-1} m^2.

In 2008–2011, we have taken samples of mushrooms and berries in the territory within a radius of 30–35 km from the PA “Mayak.” In all the samples of mushrooms, the specific activity of ^{137}Cs and ^{90}Sr was significantly below the maximum permissible levels (SanPiN2.2.2.1078-01). The activity of ^{137}Cs in 2008–2011 was from 0.55 to 39.0 Bq kg^{-1}, and MPL was 500 Bq kg^{-1}

Table 8 Contamination of ^{90}Sr and ^{137}Cs wood and birch leaves

Test	Specific activity, Bq kg^{-1}		C_a		C_t	
	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
Leaves	119	6.5	1.00	0.126	8.32	1.054
Branches	63.3	15	0.53	0.292	4.42	2.433
Trunk	32.4	6	0.27	0.117	2.26	0.973

Table 9 Contamination of ^{90}Sr and ^{137}Cs fresh mushrooms on EURT

Place of selection of test (distance from Chelyabinsk in km)	Test	Specific activity, Bq kg^{-1}		C_a		C_t	
		^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
99	1	0.47	0.58	0.0039	0.0113	0.0328	0.0941
	2	1.2	0.97	0.0101	0.0189	0.0839	0.1573
	3	0.7	0.9	0.0059	0.0175	0.0489	0.1460
100	1	0.34	4.6	0.0041	0.0176	0.0305	0.1447
	2	0.59	19.9	0.0071	0.0762	0.0529	0.6259
	3	0.63	18.5	0.0076	0.0709	0.0565	0.5819
	4	1.4	8.2	0.0169	0.0314	0.1255	0.2579
102	1	0.7	3.9	0.0092	0.0169	0.0749	0.1383
104	1	1.7	18.8	0.0531	0.0450	0.2798	0.3705
The wood near the Lake Alabuga	1	9.8	39.0	0.0017	0.124	0.0133	0.9476
	2	9.0	1.43	0.0009	0.0035	0.004	0.0145
On a place of the former village Russian Karabolka	1	5.5	10.9	0.0065	0.0586	0.0396	0.4950
	2	8.9	2.0	0.0106	0.0108	0.0641	0.0908

(SanPiN2.2.2.1078-01). The average accumulation coefficient of ^{137}Cs in mushrooms in 2011—0.011 (in 2008—0.011, 2009–2010 the samples of mushrooms were taken from a large area and the accumulation coefficient was not calculated). The activity of ^{90}Sr was from 0.14 to 9.8 Bq kg^{-1}, and MPL was 50 Bq kg^{-1} (SanPiN2.2.2.1078-01). The average accumulation coefficient of ^{90}Sr in mushrooms in 2011 was 0,007 (in 2008, it was 0.041). C_a and C_t of ^{90}Sr in mushrooms are considerably lower than in the grass, and even lower than those in vegetables and cereal crops. C_a and C_t of ^{137}Cs in mushrooms are higher than of ^{90}Sr, but in the studied area, high levels of soil contamination with ^{137}Cs occur only on the floodplain bogs in the Techa River headwaters. We can assume that the mushrooms are not dangerous for the population; their contribution to the dose of internal irradiation is negligible.

Table 9 shows the values of the specific activity of ^{90}Sr and ^{137}Cs in mushrooms collected in the territory of EURT. Since mushrooms picked in the area of former village Russkaya Karabolka and the Lake Alabuga, and in areas with contamination density of 140, 700 and 2,400 kBq^{-1}m^{2} have accumulated 8.9, 9.0, and 9.8 Bq kg^{-1} of ^{90}Sr, it is possible that under certain conditions, there may be mushrooms that do not meet sanitary–hygienic standards. In the other territory

Table 10 Contamination of ^{90}Sr and ^{137}Cs of berries on EURT

Place of selection of test	Species	Specific activity, Bq kg^{-1}		C_a		C_t	
		^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
The wood near the Lake Alabuga	Wild strawberry	813	5.2	0.140	0.0165	1.10	0.126
	Stone bramble	243	2.4	0.042	0.0076	0.33	0.058
On a place of the former village Russian Karabolka	Wild strawberry	213	1.0	0.254	0.0054	1.53	0.045

(outside EURT), wild mushrooms from the areas of now existing settlements can be considered as harmless.

In the whole area of study, the specific activity of ^{137}Cs in 15 samples of wild berries (Fragaria viridis, Fragaria vesca, cranberries) in 2008–2011 ranged from 0.34 to 5.2 Bq kg^{-1}, on the average, it was 1.58 Bq kg^{-1}, and MPL was 160 Bq kg^{-1} (SanPiN2.2.2.1078-01). The activity of ^{90}Sr in berries outside EURT was also low—from 1.5 to 12 Bq kg^{-1}, on the average, it was 5.5 Bq kg^{-1}, and MPL was 60 Bq kg^{-1}(SanPiN2.2.2.1078-01). The accumulation coefficients of ^{137}Cs in berries are almost the same as in mushrooms, and the accumulation coefficients of ^{90}Sr are significantly higher than in mushrooms and greater than in vegetables and cereal crops. In the berries of Fragaria vesca near the Lake Alabuga, the activity of ^{90}Sr in 2008 was 813 Bq kg^{-1}, and in the bramble, it was 243 Bq kg^{-1}. In the area of the former village of Russkaya Karabolka in a mixture of berries of Fragaria vesca and Fragaria viridis, the ^{90}Sr activity was 213 Bq kg^{-1}. It should be considered that wild berries from the territory of EURT pose the greatest danger from the perspective that ^{90}Sr enters into food. It is necessary to examine the nature of ^{90}Sr accumulation in berries more closely (Table 10).

3.4 Study of the Soil Content of Radionuclides Forms that are Available for Plants

Long-term studies of various authors prove that the soil content of ^{137}Cs and ^{90}Sr in forms that are available for plants changes over time. Their accumulation coefficients in the marketable part of agricultural products change accordingly. In particular strongly expressed is the decrease in mobility of radionuclides in the first years after the accident.

The studies of the behavior of radionuclides in soils show that a significant part of ^{90}Sr and ^{137}Cs changes quite rapidly into immobile forms. An immobile form is a form in which the radionuclide is bound in the root systems of plants or soil adsorption complex as a result of adsorption and precipitation (EMCRA 2001).

Table 11 The contents in the soil of forms ^{90}Sr available to plants in percentage

Soil	Layer, m^2	Soluble in water	Capable to an exchange	Soluble in acid	Insoluble
Gray forest soil, the natural	0–5	3.4 ± 0.3	67.2 ± 2.4	21.8 ± 2.1	7.61 ± 0.07
	5–10	3.9 ± 0.5	63.6 ± 4.2	25.6 ± 3.2	6.9 ± 0.6
Gray forest soil, the dried up	0–5	5.0 ± 1.2	64.3 ± 1.6	23.6 ± 0.8	7.1 ± 2.0
	5–10	1.7 ± 0.4	65.0 ± 7.5	26.5 ± 8.6	6.8 ± 1.6
Sod-podzolic soil, the dried up	0–5	2.9 ± 0.4	77.2 ± 2.4	14.2 ± 1.2	5.7 ± 0.8
	5–10	2.2 ± 0.4	85.3 ± 2.7	8.9 ± 2.5	3.6 ± 0.2

Table 12 The contents in the soil of forms ^{137}Cs available to plants in percentage

Soil	Layer, m^2	Soluble in water	Capable to an exchange	Soluble in acid	Insoluble
Gray forest soil, the natural	0–5	5.0 ± 0.7	2.7 ± 0.5	2.8 ± 1.4	89.4 ± 2.4
	5–10	13.7 ± 6.4	16.5 ± 5.4	36.6 ± 14.4	33.1 ± 7.5
Gray forest soil, the dried up	0–5	2.8 ± 0.5	10.8 ± 1.4	4.3 ± 2.0	82.1 ± 2.6
	5–10	16.5 ± 1.4	17.9 ± 5.3	16.2 ± 5.8	49.4 ± 4.2
Sod-podzolic soil, the dried up	0–5	9.8 ± 1.7	16.1 ± 8.1	17.4 ± 7.3	56.7 ± 16.6
	5–10	13.8 ± 2.9	22.6 ± 5.1	36.0 ± 6.6	27.5 ± 7.9

Since the processes of adsorption and precipitation are reversible, the ratio of mobile and immobile forms is determined by the ratio of the speed of bonding and release of radionuclides. The elements bound in the root system and aboveground biomasses are released as far as plant litter decomposes. Elements bound in the soil adsorption complex move into the soil solution as a result of exchange reactions.

We have previously shown that in case of simulation of the washing water regime for a long time, the release of radionuclides from the alluvial soil with gravitational waters ranged from 10.8 to 12.4 % of the contained ^{90}Sr and from 0.08 to 0.52 % of ^{137}Cs.

In 2008, we measured the content of water-soluble, exchange, and acid-soluble forms of ^{90}Sr and ^{137}Cs in the gray forest and sod-podzolic soil. We compared the content of bioavailable forms in layers of 0–5 and 5–10 cm in a naturally moist and air-dry gray forest soil, air-dry gray forest soil, and sod-podzolic soil. The results are shown in Tables 11 and 12.

We failed to reveal significant differences of content of biologically available forms of strontium in the studied samples of naturally moist and air-dry gray forest soil. There are also practically no differences between layers of 0–5 and 5–10 cm. It was found that in the sod-podzolic soil, the content of exchange form is higher and the content of acid-soluble form is lower than in the gray forest soil.

The content of bioavailable forms of ^{137}Cs varies more. In naturally moist gray forest soil in comparison with air-dry soil, the content of exchange form is decreased slightly in a layer of 0–5 cm. In the sod-podzolic soil higher is the content of acid-soluble form of ^{137}Cs. However, the greatest differences were observed not between the soil types, but between the layers of 0–5 and 5–10 cm. In

Table 13 Release of water-soluble radionuclides from the inundated soil at different modes of extraction, percentage of the grass

Variant	Condition of the soil	^{137}Cs	^{90}Sr
Extracted three times. a soil and water 1:15 ratio	The dry	1.21 ± 0.10	3.4 ± 0.7
	The damp	2.37 ± 0.21	6.0 ± 0.1
Extracted one time. a soil and water 1:200 ratio	The dry	0.73 ± 0.18	3.8 ± 0.04
	The damp	3.68 ± 0.31	3.4 ± 1.3
Extracted one time. a soil and water 1:30 ratio, centrifuged	The dry	0.24 ± 0.1	1.8 ± 0.6
	The damp	1.6 ± 0.4	2.8 ± 0.4
Extracted one time. a soil and water 1:30 ratio, did not centrifuge	The damp	2.7 ± 0.9	4.3 ± 1.9

all cases, the content of bioavailable forms of ^{137}Cs is higher in the 5- to 10-cm layer and the content of strongly bound forms that remain in the solid residue is significantly lower in this layer. Perhaps a high content of mobile forms explains the sharp decline in contamination with ^{137}Cs of this layer, with the assumption that in the underlying soil layer goes more ^{137}Cs than ^{90}Sr. We also compared different modes of extraction of ^{90}Sr and ^{137}Cs with distilled water from the floodplain soil.

It follows from Table 13 that the amount of ^{137}Cs extracted with distilled water from the floodplain soils when using the normal mode of extraction is lower than from the automorphic soils (gray forest and sod-podzolic soil). Apparently, this is due to the fact that the waterlogged floodplain soil quickly loses water-soluble forms of ^{137}Cs. The content of radionuclides in the aqueous extract, as was to be expected, depends on the extraction mode and soil condition. When using dry soil, we observed statistically significant differences in the amount of ^{137}Cs extracted in the ratio of 1:15, 1:30, and 1:200. The greatest amount of ^{137}Cs is extracted in case of threefold rinsing, although the amount of water in this variation is the least. Apparently, in case of long 3-h mixing takes place a more intensive dispersion of soil particles.

Quantity of ^{90}Sr extracted in the ratio of 1:15 and 1:200 does not vary, but it is significantly statistically greater than when extracting in the ratio of 1:30.

When moist soil is used, the amount of ^{137}Cs extracted in different modes is also statistically different. The extraction was the best at the ratio of 1:200 and the worst at the ratio of 1:30. It is important to note that from the moist soil in all modes of extraction was released 2–6 times more ^{137}Cs than from the dry soil. The differences are statistically significant. For ^{90}Sr, this dependence is less expressed, and at the ratio of 1:200, differences between moist and dry soil were not observed at all.

To study the possibility of recovery of content of water-soluble fractions of ^{137}Cs and ^{90}Sr when moistening the dried soil, we used the same soil sample that was used for the determination of content of water-soluble fractions of ^{137}Cs and ^{90}Sr. The results of analysis of aqueous extracts are shown in Table 14.

It follows from Table 14 that when soil is moistened during 1–16 days, there is no recovery of water-soluble ^{137}Cs. The quantity of extractable ^{137}Cs after

Table 14 The content of radionuclides in the inundated soil and water extracts from the inundated soil after drying and moistening, percentage of the contents in the soil

Variant	^{137}Cs	^{90}Sr
Natural soil	1.6 ± 0.4	2.8 ± 0.4
The dried-up soil	0.24 ± 0.1	1.8 ± 0.6
The soil dried up and humidified within 1 day	0.46 ± 0.3	3.4 ± 1.3
The soil dried up and humidified within 2 day	0.34 ± 0.03	2.04 ± 0.5
The soil dried up and humidified within 4 day	0.42 ± 0.1	2.12 ± 0.2
The soil dried up and humidified within 8 day	0.53 ± 0.13	1.6 ± 0.3
The soil dried up and humidified within 16 day	0.48 ± 0.06	1.6 ± 0.2

moisturization is slightly higher than when the dry soil is used. When soil is moistened during 4–16 days, this difference is statistically significant. When soil is moistened during 1 day, the amount of extractable ^{90}Sr is apparently restored. In the future, it reduces. The mechanism of this phenomenon is not entirely clear. We attempted to estimate the amount of ^{137}Cs and ^{90}Sr that enter into an aqueous solution of soil in case of a longtime continuous extraction.

The soil sample was collected from the 0–20 cm layer of alluvial meadow bog soils in the floodplain of the Techa River. In the moist condition, the soil was rubbed through a 0.5-mm sieve to remove fragments of plants and large mineral particles, thoroughly mixed and divided into two parts.

Part 1 (S—sterilized) was irradiated in the wet condition at a dose of 2,800 Gy (70 h at a dose rate of 0.011 Gy s^{-1}) to kill microorganisms. Part 2 (US—unsterilized) was not irradiated. From each part in the wet condition were made three different samples, 10 g each, and they were put into centrifuge tubes. In the tubes were added 50 ml of distilled water, and then, they were stirred for 60 min on a magnetic stirrer, then centrifuged for 60 min at the velocity of 2,500 rpm, and then poured off and filtered the supernatant fluid. To the rest of soil again were added 50 ml of water, and the cycle was repeated. Three cycles were made during 1 day. After 60 cycles, into the collected filtered supernatant were poured up to 5 l of distilled water, and it was stirred and separated into two parts.

In one part, we precipitated colloids using $FeCl_3$ (0.2 g l^{-1}) and filtered them in 1 day. Thereafter, we measured the content of ^{90}Sr and ^{137}Cs in the filtrate after precipitation of colloids (F), in the colloids sediment (C), and in the second part of supernatant liquid with unprecipitated colloids (NPC).

The quantity of ^{137}Cs and ^{90}Sr that entered into aqueous solution during 60 cycles is shown in Table 15.

From Table 15 follows that when using this method of extraction, about 12–20 % of ^{90}Sr and ^{137}Cs contained in soil can move into aqueous solution. Differences between the release of radionuclides from sterilized and unsterilized soil were not found. ^{90}Sr does not practically precipitate with colloids and, apparently, moves primarily into regular solution in ionic form. ^{137}Cs precipitates almost completely, and there are reasons to assume that in the extract it is in the form of a colloidal solution.

Table 15 Relative quantity of ^{137}Cs and ^{90}Sr arrived in water solution for 60 cycles. Percentage of the initial contents in the soil

Variant	Fraction	^{137}Cs	^{90}Sr
Sterilized	NPC	18.9 ± 2.4	12.0 ± 4.2
	F	0.49 ± 0.14	12.0 ± 3.3
	C	18.1 ± 1.0	1.6 ± 1.8
Unsterilized	NPC	19.4 ± 0.5	15.2 ± 4.4
	F	0.53 ± 0.16	12.1 ± 4.9
	C	17.7 ± 4.0	0.98 ± 0.3

4 Conclusion

1. The content of ^{90}Sr and ^{137}Cs in agricultural products and forest mushrooms in the entire territory within a radius of 30–35 km from the PA "Mayak" does not exceed the maximum permissible levels and poses no danger to the population.
2. The accumulation of ^{90}Sr in wild berries and grass on the territory of EURT may be higher than the radiation-hygienic standards and poses a danger to the population and farm animals.
3. The content of ^{90}Sr and ^{137}Cs in the soil in the form that is available for plants depends on soil moisture and can vary considerably.

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Migration of ^{90}Sr and ^{137}Cs in the Soil After Radiation Accidents

N. N. Kazachonok and I. Y. Popova

Abstract Studying the principles of vertical migration and radionuclides distribution in soil is essential for a prediction of their transport dynamics into the root uptake area as well as for the planning of measures for decreasing contamination of agricultural and forest goods. A study of ^{90}Sr and ^{137}Cs distribution in a soil profile, as a result of radioactive contamination due to operation of radiochemical plant, Production Association (PA) "Mayak" was carried out on the territory of northeastern part of Chelyabinsk region in 2008–2012. In forest and meadow soil, the bottom part of forest litter and the upper soil layer (0–5 cm) are the most contaminated with ^{90}Sr and ^{137}Cs. The radionuclides contamination at a depth $>$20 cm is nearly undistinguishable for different soil types. In alluvial swamp soil, ^{90}Sr is distributed through the whole soil profile, whereas ^{137}Cs is concentrated in the depth of 20–40 cm. Annual plant fallout contributes to a lower extent into contamination of the litter and upper soil layer. In the experiment with a decay of plant fallout, a ^{90}Sr distribution and contamination level in the profile of a model soil was similar to a natural soil, whereas a ^{137}Cs contamination was 10 times lower for the model soil. In the forest-steppe area of Chelyabinsk region, a change of an upward and downward water flow in soil takes place several times in a season, during certain years a fallout and evaporation vary a lot. That is the reason for constant and unpredictable change of vertical radionuclides migration. A computer program for imitation modeling of radionuclides mobility in soil has been developed in our group. The radionuclides behavior in soil is determined by a probability of decay during certain period of time and by a probability of transport up and down within profile for a different distance independent of displacement mechanism. In a certain period of time, a position of a radioactive particle is defined by the sum of opposite directed vectors, each of which in a natural stochastic system is randomly determined, considering probabilities characteristic for given natural system.

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Contents

1 Introduction

The radioactive contamination of the soil is caused in the most cases by the aerosol fallout from the atmosphere. At first are contaminated the soil surface and the aerial parts of plants. The radionuclides migrate gradually and divide in the whole thickness of the soil layer. The study of the regularities of vertical migration and distribution of radionuclides is necessary for forecasting the dynamics of their transfer to the root absorption zone and for planning the measures aimed at the lowering of agricultural and forest products contamination.

The multiyear activity of Production Association “Mayak” has resulted in radioactive contamination of soils in Transurals. The discharges in the air, waste tank explosion in 1957 East-Ural radioactive trace (EURT), carrying away of Karachay lake silt by the wind in 1967 (Karachay Trace) led to the fallout of radioactive aerosols on the soil surface. In the years 1949–1956, the liquid radioactive waste has been disposed in the River Techa and it resulted in the floodplain soil contamination.

Therefore, there are unique conditions in the Transurals for researching the regularities of radionuclides migration in a long-term period by different circumstances of radioactive contamination.

2 Materials and Methods

The researches have been conducted in 2008–2012 in the territory of northeastern part of Chelyabinsk region that suffered from radioactive contamination caused by the activity of radiochemical industrial complex of the Production Association "Mayak." For the analysis of radionuclides distribution dynamics in the soil profile, we used the materials from the database of Urals Research Center for Radiation Medicine.

The specific activity of ^{137}Cs was measured by means of scintillation gamma-ray spectrometer with the software "Progress." From 2011, the spectrometer facility MKC-01A "MULTIRAD" was used for this purpose. In the low-activity samples of ^{137}Cs, the radiochemical iodine-antimony method after concentrating it on the nickel ferrocyanide was used for the measurements. The specific activity of ^{90}Sr in the samples was measured by means of the extractive method based on daughter ^{90}Y using monoisooctyl methylphosphonate. The ß-activity of the selected radionuclides was measured using low-background radiometric facilities УМФ-1500 and УМФ-2000 with flame-photometric control of strontium carrier yield. The method for measuring ^{239}Pu is based on concentrating and cleaning of plutonium isotopes on the anion exchange resin and the following electrochemical deposition on the steel disks. The α-activity was measured using the α-spectrometer facility based on pulsed ionization chamber. The specific activity of plutonium isotopes in the samples was identified and measured on the basis of radiation energy and intensity, using marking (^{236}Pu or ^{242}Pu) with the known activity that was previously brought into the samples. All applied methods and measuring means have State calibration certificates.

3 Results and Discussion

3.1 The Study of Vertical Migration of ^{90}Sr and ^{137}Cs in Automorphic Soils of Terrestrial Ecosystems

In 2008–2011 were taken the samples of soil and ground litter in 130 points of terrestrial ecosystems from the areas of 52 currently existing and 2 evacuated settlements. Virtually in all points where samples were taken the upper soil layer and the forest litter (in the meadow soil–sod cover or steppe mat) were most contaminated by ^{137}Cs and ^{90}Sr. The ratio of the specific activity of radionuclides in the 0- to 10-cm layer to the activity in the 10- to 20-cm layer did not depend on the total contamination density. The value of this ratio is influenced by the type of the ecosystem to the maximum extent: in the forest ecosystems, this ratio for ^{137}Cs is on the average 20.4 ± 4.4, in the meadow ecosystems 2.9 ± 1.6 (although there are exceptions). For ^{90}Sr, the differences are insignificant: 3.4 ± 0.9 in forest, 2.8 ± 1.5 in meadow.

The ratio of the specific activity of ^{137}Cs in the litter to the activity in the 0- to 10-cm soil layer was on the average 0.5 ± 0.1, ^{90}Sr 1.5 ± 0.2. Although the specific activity of ^{137}Cs and ^{90}Sr in the litter is pretty high, it has little effect on the total contamination density, as the litter bulk density is by 2 orders lower than the soil bulk density. Consequently, the importance of the litter in the radionuclide accumulation is significantly lower for the Transurals soils than for forest soils of Polessky radiation reservation that was contaminated as a result of the Chernobyl accident. In the soils of Polessky radiation reservation, the activity of ^{90}Sr and ^{137}Cs in the litter is about 10 times higher than in the upper soil layer. Accordingly, in the litter is deposited 39 % of the total content of ^{90}Sr in the profile up to a depth of 105 cm. The content of ^{137}Cs is 55 % (Mashkov and Malenok 2008).

While analyzing the pattern of ^{90}Sr distribution in the soils of EURT at different times after the accident, it was found that in forest soils in the 50 years that have passed since the accident the contamination maximum practically was not transferred from the 0- to 5-cm layer (Fig. 1a, b). There was a more balanced distribution of ^{90}Sr in the soil profile of the black earth, what is obviously connected with the replowing (Fig. 1c).

The distribution of ^{90}Sr in the profile of a 30-cm layer is well described by the exponential function $y = ae^{-bx}$, where y is the content of radionuclide in the layer (% from the total contamination density a 30-cm layer), x is the ordinal number of a 5-cm layer. The determination coefficients of R^2 approximating curves for gray forest soil, and in the initial period after the accident for soddy-podzolic soil and black earth too, are pretty high (Kostyuchenko et al. 2012a, b). In the remote period after the accident the elective accumulation of ^{90}Sr in particular layers of soddy-podzolic soil increases, this is apparently connected with the inhomogeneity of physicochemical properties. The ^{90}Sr distribution inhomogeneity in the profile of black earth is explained by the mechanical replacement of a part of the radionuclide while processing. Of the greatest interest is the coefficient b using which can be calculated the depth where the contamination density decreases up to the specified multiplicity. ^{90}Sr settled on the soil surface migrates slowly into the deeper layers and the coefficient b decreases. Especially, good this ratio can be seen at the gray forest soil: the coefficient b correlates with the number of years after the accident ($r = -0.949$, $p = 0.02$). ^{90}Sr migration in the soddy-podzolic soil goes more intensive. Such soil is formed at higher moisture; coniferous plant litter contains a lot of organic acids that promote leaching of related elements. The ^{90}Sr distribution pattern in the black earth profile was mostly influenced by the replowing in 1960–1990. The values of b for these soils decrease faster, but the dependence of b on the time is less expressed: for the soddy-podzolic soil $r = -0.68, p = 0.20$; for the black earth $r = -0.79, p = 0.11$.

The distribution of ^{137}Cs and ^{90}Sr in the soil profile was studied more detailed on the EURT axis (20, 30 and 55 km from the industrial site) and to the south of the Production Association "Mayak" (7, 10 and 20 km from the industrial site). The distribution of ^{90}Sr and ^{137}Cs in the soil profile was examined for 3 types of soil: gray forest soil, soddy-podzolic soil and black earth. The results can be found in Table 1. As Table 1 shows that, although the types of soils, the sources of

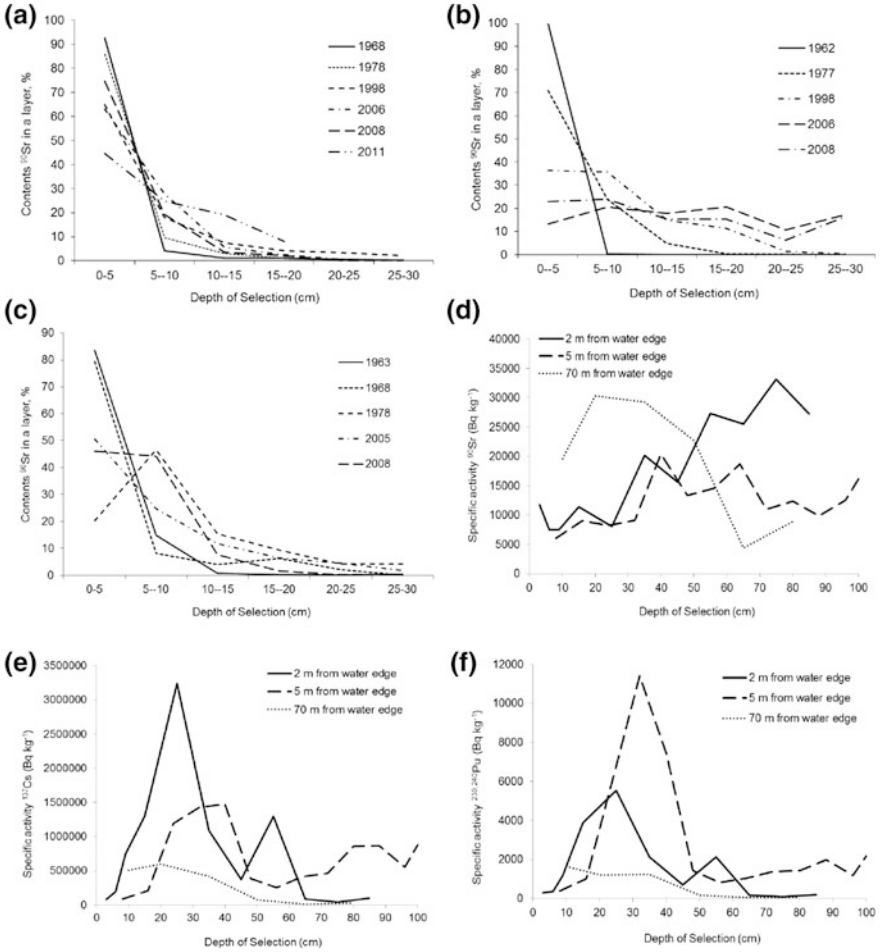

Fig. 1 **a** Dynamics of distribution of ^{90}Sr on a profile of the gray forest soil. **b** Black earth soil. **c** Soddy-podzolic soil. **d** Marsh soil. **e** Distribution of ^{137}Cs on a profile of the marsh soil. **f** Distribution of ^{239,240}Pu on a profile of the marsh soil

contamination and the contamination density are various, the specific activity at the depth over 20 cm the specific activity of ^{137}Cs and ^{90}Sr is virtually identical.

The same specific activity of ^{137}Cs and ^{90}Sr—in the range of 9–11 Bq kg^{-1} is described for various subtypes of black earth in Orenburg region in the 20- to 50-cm layers (Efremov 2008). Apparently, the differences in activity of ^{137}Cs and ^{90}Sr that depend on the contamination nature, the contamination density and the type of soil, are observed in automorphic soils of extremely continental climate zone only to a depth of about 20 cm. Then, to a depth of 2–3 m the content of these radionuclides is the same. In the forest soils of Polessky radiation reservation, ^{137}Cs and ^{90}Sr are distributed more equally (Mashkov and Malenok 2008). It should be noted that the

Table 1 Specific activity ^{137}Cs and ^{90}Sr on a soil profile in 2008–2011

Layers in cm	Soddy-podzolic		Gray forest soil						Black earth			
	EURT (55 km)		Southern direction (7 km)		Southern direction (10 km)		EURT (20 km)		EURT (30 km)		Southern direction (20 km)	
	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr
0–5	206	1,910	480	104.3	299	95.8	479	7,809	143	30.8	25.8	33.1
5–10	12.1	1,771	27.3	48.9	192	85.5	23.2	2,029	101.5	32.2	20.1	22.0
10–15	15.2	295	16.4	23.2	26.7	33.5	8.1	363	87	20.8	19.9	17.9
15–20	10.3	57.9	15.2	33.8	5.9	11.6	13.3	223	41	20.7	13.7	20.5
20–25	8.9	10.5	11.3	17.7	12.2	6.6	6.5	12.3	13.2	8.4	12.2	3.5
25–30	6.7	6.9	9.5	2.0	3.3	6.1	6.1	16.7	10.6	22.1	8.2	8.4
30–35	17.6	17.9	3.9	1.6	8.8	2.8	4.4	14.7	12.3	5.1	5.2	14.1
35–40			5.5	0.95	5.8	5.0	9.2	12.1			4.5	2.9
40–45	12.5	14.8	10.9	7.4	6.3	7.8	22.6	15.6	15	8.7	5.8	1.4
45–50			11.3	8.9	7.3	13.4	9.7	14.0			8.2	4.6
50–55	2.4	6.6	11.6	6.1	4.1	4.6			8.7	5.0	3.9	3.9
55–60			–	–	–	–	12.7	34.6			4.5	7.1
60–65	2.4	4.1	–	–	–	–			6.6	5.3	4.1	2.0
65–70			–	–	–	–	4.2	11.1			3.9	6.6
70–75	2.2	4.3	–	–	–	–			9.9	5.0	2.7	2.9
75–80			–	–	–	–	3.5	4.7			8.2	5.3
80–85			–	–	–	–			8.8	9.7	4.7	3.1
85–90	8.6	7.9	–	–	–	–					5.6	2.7
90–95			–	–	–	–	5.5	10.6	41.3	23.2	4.6	0
95–100			–	–	–	–					5.9	10.2
100–105	6.2	8.2	–	–	–	–			10.7	7.4	4.5	3.4
105–110			–	–	–	–	9.0	6.8			7.4	6.1
110–115			–	–	–	–			–	–	3.8	0
115–120	7.6	7.3	–	–	–	–			–	–	7.6	8.6
120–125			–	–	–	–			–	–	–	–
125–150	–	–	–	–	–	–	7.8	2.8	–	–	–	–
150–175	–	–	–	–	–	–	7.4	2.9	–	–	6.5	19.9
180–185	–	–	8.8	4	–	–	–	–	–	–	–	–
295–300	–	–	10	8.5	–	–	–	–	–	–	–	–

area of Polesye has been recognized as a biogeochemical province with high mobility of ^{137}Cs long before the Chernobyl accident (Alexachin and Tichomirov 1976).

Significant influences on the radionuclides distribution pattern in the soil profile have agro technical measures. In 2007, in the vegetable rotation fields of «Sovkhoz Beregovoy» LLC in 47 % cases on the irrigated lands and in 19 % cases on the bogharic lands the 20- to 40-cm subsurface layer contained more radionuclides than the 0- to 20-cm top soil layer (Table 2).

Table 2 The relation of density of pollution of arable and sub-arable layers (0–20 cm/20–40 cm) on fields of a vegetable crop rotation

Cultivation conditions	^{90}Sr	^{137}Cs
Watering	1.4 ± 0.6	1.3 ± 0.9
Not watering	1.8 ± 0.3	2.2 ± 0.9

3.2 The Study of Vertical Migration of ^{90}Sr and ^{137}Cs in Hydromorphic Soils of Floodplain

The floodplain of Techa River is contaminated with radionuclides due to the discharges of liquid radioactive waste in 1950–1956. The soil in the river headwaters is polluted to the maximum extent. Figure 1d–f shows the radionuclides distribution in the profile of the bog soil from the selection place in the area of Asanovsky bogs, 7.5 km away from the dam of B-11 technical water reservoir. Figure 2a–c shows the radionuclides distribution in the profile of the meadow Soddy soil, 24 km away from the dam of B-11 water reservoir. It can be seen that in the bog soil and in the bank Soddy soil that are constantly wet, ^{90}Sr migrates to a greater depth and is accumulated in different layers. ^{137}Cs and ^{239,240}Pu migrated in the bog soil up to the depth of 100 cm, but the largest number of them is contained in the 20- to 40-cm layer. In the Soddy soil, ^{137}Cs and ^{239,240}Pu remained mainly in the surface layer. These differences have to be taken into account while assessing the territory contamination density and calculating the total supply of radionuclides.

While comparing the specific activities of radionuclides in the samples, it was found that the horizontal and vertical distribution of ^{137}Cs and ^{239,240}Pu in the soil is similar. For 352 soil samples taken at different sites along the bed, at different distances from the river and at different depths, the correlation coefficient between the activities of these radionuclides equaled to 0.869 (Fig. 2d). The dependence of activities of ^{137}Cs and ^{239,240}Pu in the bottom silt was lower, the correlation coefficient—0.688 for 176 samples (Fig. 2e). These relations enable us to assess approximately the ^{239,240}Pu contamination level based on the results of γ-spectrometric measurement of ^{137}Cs. The equation for the soils: $A_{Pu} = 0.044\ (A_{Cs}^{0.73})$; A_{Pu} and A_{Cs}—specific activities of ^{239,240}Pu and ^{137}Cs ($R^2 = 0.816$); for the bottom silt—$A_{Pu} = 0.033\ (A_{Cs}^{0{,}78})$, ($R^2 = 0.847$).

The correlation coefficients between the activities of ^{137}Cs and ^{90}Sr, ^{90}Sr and ^{239,240}Pu in all taken samples are also statistically significant, but low (from 0.30 to 0.52). This is explained by the fact that the behavior of ^{90}Sr in the soils differs from ^{137}Cs and ^{239,240}Pu. During the time that has passed since the massive discharges of radionuclides the correlation between the radionuclides has changed.

Therefore, only the samples taken at the earliest in 2007 were chosen for the calculation of the equation for calculating the activity of ^{90}Sr using the dates on the activity of ^{137}Cs. Figure 2f shows the relation of specific activities of ^{90}Sr and

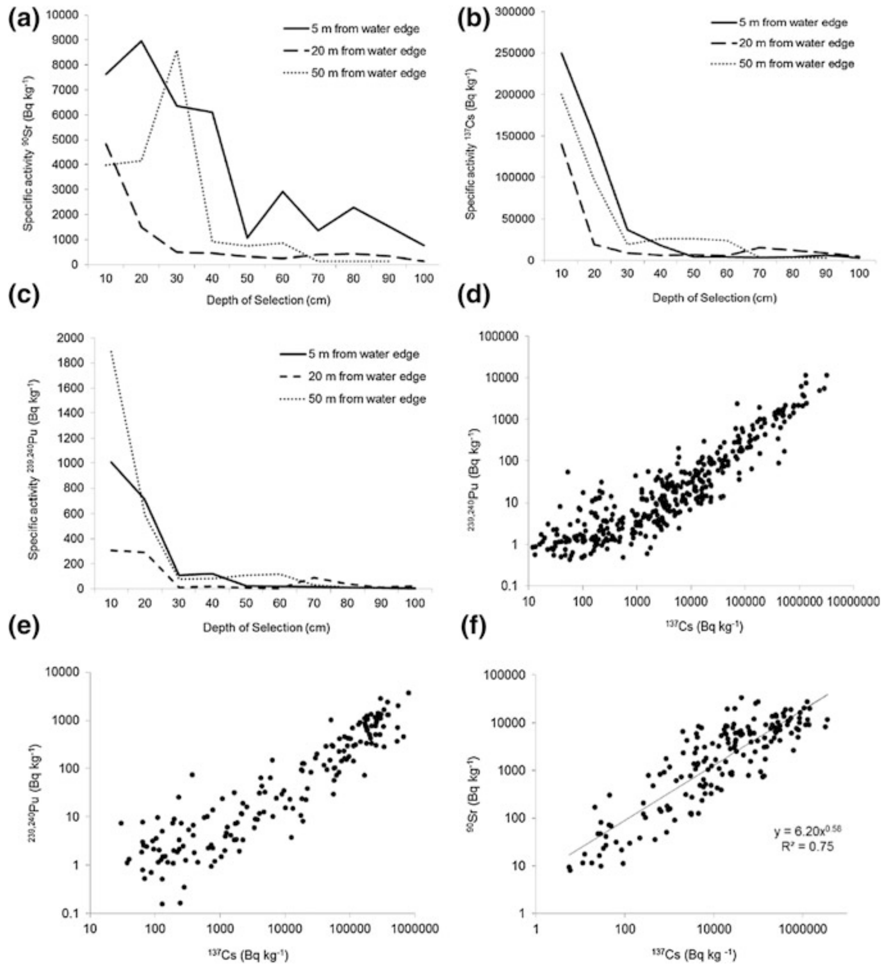

Fig. 2 **a** Distribution of ^{90}Sr on a profile of the cespitose meadow soil. **b** Distribution of ^{137}Cs on a profile of the cespitose meadow soil. **c** Distribution of ^{239,240}Pu on a profile of the cespitose meadow soil. **d** Correlation of specific activity of ^{137}Cs and ^{239,240}Pu in samples of inundated soils. **e** Correlation of specific activity of ^{137}Cs and ^{239,240}Pu in samples of ground deposits. **f** Correlation of specific activity of ^{137}Cs and ^{90}Sr for all samples

^{137}Cs in soil samples taken from different depths. Figure 3a shows information about the samples taken from the upper layer. The approximating curves equations and determination coefficients can be seen on the same figures.

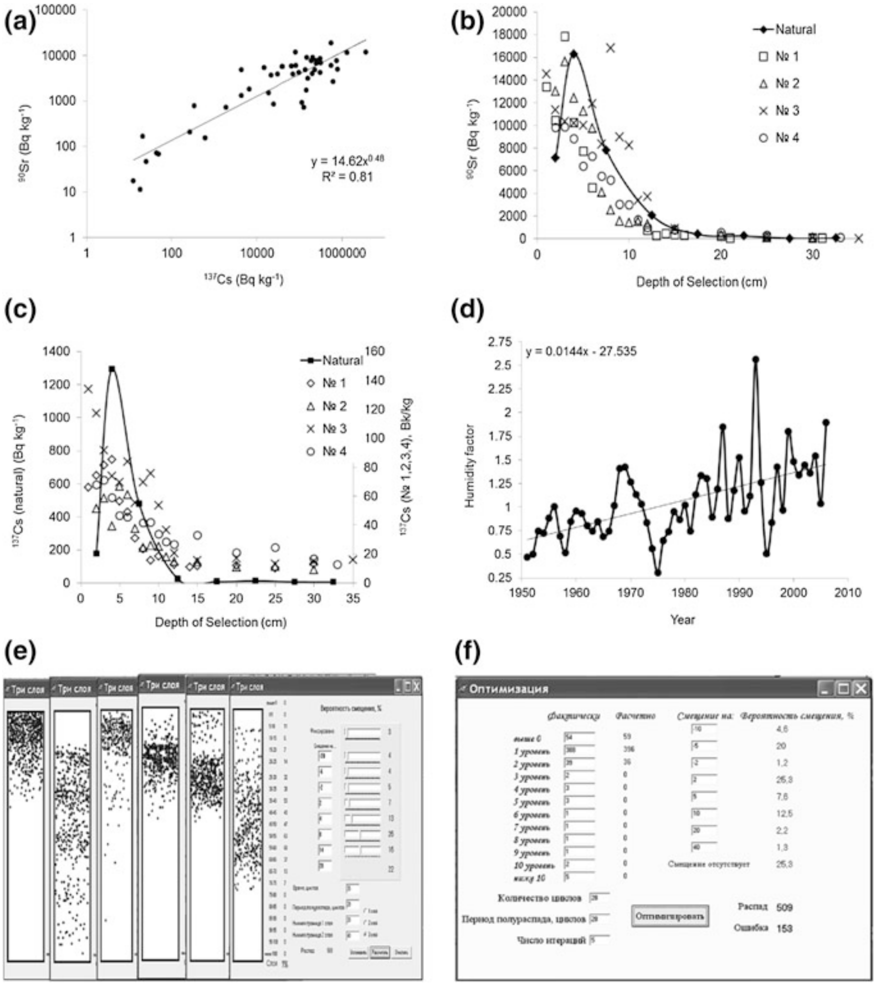

Fig. 3 **a** Correlation of specific activity of ^{137}Cs and ^{90}Sr in soil samples from a layer of 0–10 cm. **b** Specific activity of ^{90}Sr in the soil after decomposition of the remains of plants. **c** Specific activity of ^{137}Cs in the soil after decomposition of the remains of plants. **d** Dynamics of humidity factor. **e** Examples of the distributions received at modeling of a local circulation of radionuclides. **f** Result of optimization of values of probabilities of shift of radionuclide

3.3 Regularities of Local Circulation of Radionuclides

The most researchers, who studied the distribution of radionuclides in the soil, note that in the first years after atmospheric fallouts the greatest specific activity of ^{90}Sr and ^{137}Cs is observed in the sod cover or in the forest litter. However, it is known that the plant litter formed by the grass decomposes during one season and the leaf forest litter–during 3–4 years. A little longer decomposes the coniferous forest litter, but in 50 years that have passed after the formation of EURT the forest litter that was contaminated by atmospheric fallouts had to decompose a long time ago and the steppe mat of the black earth began to form at the earliest in 1991. Thus, the high specific activity of the litter observed at the moment in the territory of EURT is determined not by primary fallouts of 1957 and even of 1967, but ether by a high speed of local circulation of radionuclides, or by the ongoing atmospheric fallouts of production waste from the Production Association "Mayak."

The supply of radionuclides in the litter and in the upper soil layer is constantly refilled with the plant litter. This litter is in its turn contaminated by atmospheric fallouts and due to the transfer of the radionuclides to the top by the root system. By virtue of the fact that the over ground biomass of the grass transforms to the litter at the end of the year almost completely, the annual transfer of ^{90}Sr to the surface is determined by annual productivity of the ecosystem.

The litter formed by the woody plant formation makes only one part of annual gain, apart from the leaves and the grass the litter consists of slowly decomposing wood, needles and cones. That is why the radionuclides are deposited not only in the soil, but also in the wood and in the litter. When the dead biomass is mineralized, the relative content of radionuclides in the litter increases.

In the territory of EURT, the ratio of the specific activity of ^{90}Sr in the grass to the activity in the 0- to 10-cm soil layer 20 km away from the Production Association "Mayak" was 0.7 ± 0.3, 30 km away 2.1 ± 1.0. For ^{137}Cs is this ratio accordingly 0.08 ± 0.04 and 0.4 ± 0.4. Since the grass is relatively more contaminated on a greater distance, we can assume that now prevail the entry of ^{90}Sr and ^{137}Cs to the biomass through the roots.

In 2008, on the axis of EURT 20 km away from the Production Association "Mayak" the plant litter from the current year was collected in the birch forest. The specific activity of ^{90}Sr in the litter amounted to 5,904 Bq kg^{-1} and ^{137}Cs 54 Bq kg^{-1}. With the litter of over ground phytomass, 2.3 kBq m^{-2} ^{90}Sr and 0.28 kBq m^{-2} ^{137}Cs were transferred to the surface of the soil (litter). This amounted to 2.1 % of ^{90}Sr and 3.4 % of ^{137}Cs of the contamination density of the whole forest litter layer and to 0.36 % of ^{90}Sr and 0.8 % of ^{137}Cs of the total contamination density of the litter and the 0- to 20-cm forest layer. Consequently, the plant litter of the aboveground organs provides a small proportion of contamination density of the litter and the upper soil layer.

Table 3 shows the values of the specific activity of radionuclides in the litter and the upper soil layer. Activity of ^{90}Sr in the upper part of the litter coincides virtually with the activity in the upper soil layer; the activity in the lower part is considerably higher. The activity of ^{137}Cs in the upper and lower layers of the litter differs to an even greater degree, than the activity of ^{90}Sr.

The specific activity of ^{90}Sr in the litter was higher than in the grass at a distance of 20 km from PA"Mayak" 2.2 ± 0.7-fold, 30 km 6.4 ± 3.6-fold; of ^{137}Cs- 14 ± 8-fold and 12 ± 8-fold accordingly. Question arises by which mechanisms is maintained a high specific activity in the lower layer of the soil litter.

Table 3 Activity of radionuclides in the soil and a lying in EURT territory (kBq kg^{-1})

Distance from Mayak PA (km)	Soil	Top part of a laying		Lower part of a laying		Layer of earth (0–5 cm)	
		^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
20	Gray forest soil	7.1	0.18	16.3	1.3	7.8	0.48
	Black earth	0.6	0.02	1.2	0.2	1.1	0.3
30	Black earth	0.03	0.005	0.09	0.02	0.03	0.14
55	Soddy-podzolic	2.8	0.06	10.0	1.2	1.9	0.2

In 2010–2011, the influence of water regime and burrowing detritophagous (*Lumbricus* sp.) on the migration of ^{137}Cs and ^{90}Sr to the soil from the contaminated plant litter was studied under laboratory conditions. The litter was collected in October 2010 in the birch forest in the area of the evacuated village Alabuga. The initial activity of ^{137}Cs in the plant litter was 180 Bq kg^{-1}, of ^{90}Sr 6,100 Bq kg^{-1}. The soil was taken from the horizon A_1 of gray forest soil that was radioactively polluted only as a result of global fallouts. The initial activity of ^{137}Cs in the soil 11.0 ± 7.0 Bq kg^{-1}, the initial activity of ^{90}Sr in the soil 7.6 ± 7.1 Bq kg^{-1}. A 35-cm soil layer was placed into the plastic cylinders with a diameter of 10 cm and with a length of 45 cm. The 5-cm high plant litter layer was placed on the soil surface. Once a week during the whole experiment, we added fresh litter in order that the litter layer equaled to 5 cm.

The experiment was carried out during 12 months in 4 variations:

No. 1.

Sprinkling of litter surface with 10 ml distilled water 3 times a week.

No. 2.

Before the litter placement 10 grown-up earthworms *Lumbricus* sp. were placed on the soil surface. Sprinkling of litter surface with 10 ml distilled water 3 times a week.

No. 3.

Sprinkling of litter surface with 50 ml distilled water 3 times a week.

No. 4.

Before the litter placement 10 grown-up earthworms *Lumbricus* sp. were placed on the soil surface. Sprinkling of litter surface with 50 ml distilled water 3 times a week.

We stopped to add the litter after 12 months. The experiment was terminated after the complete disappearance of the litter from the soil surface, the soil was divided into 1-cm-thick layers, dried and the content of ^{90}Sr and ^{137}Cs was measured in these layers. It was found after ending the experiment that there is the rest of semi decomposed litter (parts of branches) in the upper soil layers. Apparently, the detritophagous kept in the litter and soil contributed to the mixing of the branch rests with the soil.

The thickness of mixed soil layer was:

Variation No. 1–6 cm
Variation No. 2–7 cm
Variation No. 3–10 cm
Variation No. 4–10 cm

In the variations No. 3 and No. 4 have formed a washing water regime. The washing water was collected and analyzed. It was found that during the whole experiment in the variation No. 3 2.03 Bq of ^{90}Sr and 0.14 Bq of ^{137}Cs were washed away with the washing water. It were washed away in the variation No. 4 5.88 Bq of ^{90}Sr and 0.35 Bq of ^{137}Cs. Consequently, the transfer of radionuclides with the soil water was insignificant.

Figure 3b and c shows the values of specific activity of ^{90}Sr and ^{137}Cs that were transferred into the humus horizon of gray forest soil during the decomposition of plant litter collected in the birch forest on the axis of EURT. For comparison, the values of the specific activity in the natural gray forest soil in the place where the plant litter was collected are written on the same figure.

The pattern of ^{90}Sr distribution from the contaminated plant litter to the humus horizon of the gray forest soil during the 12-month-long experiment corresponds generally with the contemporary ^{90}Sr distribution in the gray forest soil of EURT. The highest specific activity was noted in the rest of the litter and in the upper soil layer. During the experiment in different moisture regimes, the average specific activity of ^{90}Sr in the 0–5-cm layer was from 0.8×10^5 to 1.2×10^5 Bq kg^{-1}. In the natural soil where the litter was collected the activity of ^{90}Sr in the lower litter part was 1.6×10^5 Bq kg^{-1}, in the 0–5-cm layer 0.8×10^5 Bq kg^{-1}.

The distribution of ^{137}Cs in experiment differed significantly from the distribution in the natural soil of EURT. In the upper litter layer of the natural soil, the activity of ^{137}Cs was 178 Bq kg^{-1}, in the litter collected for the experiment the activity of ^{137}Cs was 180 Bq kg^{-1}, in the lower litter layer of the natural soil the activity of ^{137}Cs was 1,293 Bq kg^{-1}, in the 0- to 5-cm layer of the natural soil 480 Bq kg^{-1}. And in experiment in the upper soil layers the activity of ^{137}Cs was not higher than 100 Bq kg^{-1} in most cases. But in the natural soil in the 10- to 15-cm layers and lower the activity of ^{137}Cs was 2- to 3-fold lower than in similar soil layers in experiment.

It was found while comparing the results of different variations of experiment that the moisture regime had the greatest influence on the migration of ^{90}Sr and ^{137}Cs in the soil. Many authors have noted that the most important factor in determining the mobility of radionuclides is soil moisture (Perevolotsky 2006). It should be expected that in natural conditions in the washing water regime the radionuclides migration downward the profile will increase and in the not washing regime, it will decline. In the forest-steppe zone of Chelyabinsk region, the most of precipitation falls in July in the form of showers. In May and June, the amount of precipitation is small. Thus, several times per season occurs the change of upward and downward water flows in the soil. In addition, in particular years, the amount of precipitation and evaporation capacity can vary greatly. Figure 3d shows the values of humidity factor (HF) calculated by us on the grounds of the dates from

Ozersk meteorological station (Mayak 2007). It is to see that in the initial years after the start of PA “Mayak” the water regime of automorphic soils was mostly not washing (HF < 1) and the fluctuations of HF were relatively smooth. Since 1982 there are sharp changes of HF values, in most cases HF > 1 (it corresponds to the washing water regime for automorphic soils). Therefore, the vector of radionuclides vertical migration is constantly and unpredictably changing. This uncertainty creates problems for the mathematical modeling of the vertical migration of radionuclides.

3.4 Modeling of Local Circulation of Radionuclides

Development of models was conducted till present in the following areas.

3.4.1 Analytical Models

Analytical or logical models of radionuclides migration in the soil represent functions in which the variables are the parameters of the processes and factors that influence, in the opinion of the authors of the models, the value characterizing the result of migration (speed of activity front or activity maximum replacement, a.s.o.). Initially, we considered 2 factors influencing the vertical migration: diffusive transfer, convective transfer and their combined action. The indices of the variables were then calculated empirically. Baturin (1997) has obtained a semiempirical equation for the soils of EURT using the parameters of convective transfer speed and diffusive penetration speed that he has found by exhaustion. Based on this equation, he calculated that the maximum concentration of radionuclides moves at a speed of 0.3–0.4 cm per year. At the same time in 25 years, the rate of diffusion of ^{137}Cs decreases by 0.01 cm year^{-1} and of ^{90}Sr increases by 0.02 cm year^{-1} (Baturin 1997). A fundamental study of the factors influencing these factors has performed Prochorov (1981) showed that according to the influence on the diffusion, the soil properties are arranged in a row: humidity $>$ amount of exchange calcium and magnesium $=$ exchange capacity $\Longrightarrow$ humus pH $>$ temperature. He also evaluated the role of adsorption in the migration of ^{90}Sr (Prochorov 1981).

These three models are used nowadays too. But apparently, they are suitable for a homogeneous unstructured and constantly moist soil which has been exposed to a onefold surface contamination. For most types of soil, an effective diffusion is only possible within the structural aggregate at a time when the soil is sufficiently moistened. While analyzing the convectional transfer, it is necessary to distinguish the transfer of radionuclides with gravity water and the movement in capillary pores, which can be multidirectional.

Istomin et al. (2005) have developed a model of one-dimensional vertical migration of radionuclides in a multiphase system of topsoil. The model takes into account many parameters, including soil pore tortuosity, energy release capacity during evaporation/condensation and crystallization/melting of water, as well as radioactive decay (Istomin et al. 2005). It is clear that the measurement of all these parameters in a specific soil-plant system is a very labor-intensive process. In addition, it is first necessary to define empirically in a multifactorial experiment and in natural conditions the values of the indices of equations describing the dependences of input and output parameters. Considering that an increase in the number of variables leads to an avalanche accumulation of error such models may be mainly of a theoretical interest.

3.4.2 Empirical Models

In empirical models, the available data on the specific activity or the content of the radionuclides in particular soil layers are used for calculating the spatiotemporal characteristics of migration process (speed of maximum replacement, half-residence time in the layer a.s.o.) or the predicted values of the activity or the content of radionuclides in the respective layers (Trapeznikov et al. 2007).

Several researchers calculate simply the regression equations for the actual values of radionuclide activity in soil layers. Most researchers use for this purpose an exponential function. So, Efremov (2008) has calculated the parameters of the regression equation of exponential type for ^{137}Cs and ^{90}Sr in the profile of several soil types and subtypes of the Orenburg region (Efremov 2008). Arastovich (2004) has calculated the formulas of exponential dependence of the concentration of ^{137}Cs and ^{90}Sr on the time in the soil layer of sod-podzolic swampy uncultivated soil in the Gomel and Brest regions (Arastovich 2004).

We have calculated the regression equations for the distribution of ^{90}Sr in the profile of three types of soil that are common in the territory of East-Ural Radioactive Trace and the 30-km zone of PA “Mayak” based on 5 selections of each type made at different times after the accident (between 1962 and 2008). The distribution of ^{90}Sr in the profile of a 30-cm layer is well described by an exponential function: $y = \mathrm{a}e^{-bx}$, where y—the radionuclide content in the layer as % of total contamination density of the 30-cm layer, x—the number of the 5-cm layer. ^{90}Sr fallen on the surface of the soil migrated slowly into the deeper layers and the coefficient b decreased gradually during the years passed since the accident.

For gray forest soil: the value of the coefficient b correlates with the best way with the number of years that have passed since the accident ($r = -0.94$, $p = 0.02$). b values for other soils eventually decrease over time faster, but the dependence of b on the time is less expressed: for the sod-podzolic soil $r = 0.68, p = 0.20$; for the black earth $r = 0.79, p = 0.11$. In the remote period after the accident, the selective accumulation of ^{90}Sr in particular layers of sod-podzolic soil increases, and it is apparently connected with the heterogeneity of the physicochemical properties. Heterogeneous distribution of ^{90}Sr in the profile of black earth, its accumulation above the plow pan level is explained by the mechanical transfer of a part of radionuclide during the processing (Kostyuchenko et al. 2012a, b).

3.4.3 Structural Dynamical Models

The models are based on the presentation of the ecosystem in a form of flows and levels. The information about levels is contained in databases; the flows are calculated on the basis of analytical model equations of transfer functions. In the model are used the parameters of equations that are derived empirically and are also contained in the database. Detailed models based on structural dynamical principles are developed by Mamikhin (2003). Such a model can very detailed describe the condition and behavior of an ecosystem, but requires a huge amount of actual data during the development stage. In case of lack of actual data, it is suggested to use numerical experiments with different options of functions and to assess the unknown parameters through the method of successive approximations (Mamikhin 2003).

The principles of structural dynamics are similar to the principle of neural networks used for modeling the vertical and horizontal migration of contaminants. For such models is also needed a large amount of initial information that is systematized in the form of the databases. In the models developed under the leadership of Kundas et al. (2011) are used multilayer networks. The entry layer reflects the conditions (the initial substance concentration, time, type of soil, etc.), the auxiliary layers and the auxiliary networks are used to specialize the conditions (physicochemical properties of a particular type of soil, etc.). For signal processing are generated intermediate and hidden layers. An important advantage of neural networks is their ability to self-learning. In conventional structural dynamical models various errors are accumulated when the number of structural elements increases and in the neural networks due to the “back-drive” and self-learning of the system the errors are minimized (Kundas et al. 2011).

3.4.4 Use of Virtual Machines

In our opinion, a promising direction in the modeling of the processes of contaminant transfer in a heterogeneous environment can be virtual machines that simulate the behavior of contaminant particles (ions, molecules, colloidal particles) in a heterogeneous system. Such models can be used for setting up virtual experiments for predicting the behavior of particles under the known parameters of transfer probability and for the assessment of these parameters under the known transfer result.

For example, Zhikharevich and Shumilyak (2012) have showed the congruence of temperature distribution in the sample between the cellular automaton model and the exact analytical solution of the equation of the heat transfer at a point in time (Zhikharevich and Shumilyak 2012) and also examined cellular automaton models of continuous and discrete diffusion and pointed out that the diffusion coefficient should be in the form of a probability function taking values from 0 to 1 with some degree of probability (Zhikharevich and Ostapov 2009).

A radioactive particle that is fallen on the soil surface is displaced after a certain time interval along the soil profile for the vector that is the resultant of all forces acting on the particle during this time. Whereas the soil is heterogeneous, the fate of each individual particle is determined by a number of random factors, so the particles do not move in a united front, but "spread" in the profile. Ions, colloidal micelles, isotopes connected in the crystalline grid can migrate at different speeds and in different directions. In soils without significant incline none of horizontal directions will prevail, the possibility of the horizontal displacement of a particle is equally compensated by the displacement of another particle in the opposite direction. Therefore, only vertical transfer, i.e., the projection of the resultant of all the forces acting on the vertical, should be taken into account while modeling.

The behavior of radionuclides in the soil is determined by the decay probability in a given period of time, and the probability of their displacement at various distances up or down along the profile during this period, regardless of the mechanism of displacement. After a certain number of timeslots the position of a decayed particle is determined by the result of the addition of oppositely directed vectors, each of which is defined randomly in the natural stochastic system in accordance with the probabilities that are typical for this natural system.

In our opinion, it is reasonable to use simulation modeling with cellular automata method for solving some tasks related to the study of dynamics regularities of vertical migration and distribution of radionuclides in the soil profile.

The space is discretized in the form of an array, the time—in the form of a rotation of the cycle. For the array, elements (in this case—for ions or colloidal particles) are given the rules of status change. The basic algorithm of the module on each rotation of the cycle simulates the random selection of the particle displacement vectors in accordance with the given probabilities.

Currently, we have developed, tested and tweaked in Delphi the principal algorithms of the model of radionuclide particles migration in the soil and created functional modules of this model:

1. Module that simulates the migration of particles in a homogeneous soil, with taking the decay into account. The researcher can change the displacement probabilities for different vectors and perform a complex of virtual experiments in order to study the behavior of particles, find the leading vectors and compare them with the natural physicochemical processes.
2. Module that simulates the migration of particles in a 3-layer-soil, with taking the decay into account. While working with this module, the researcher can specify arbitrary or actual values of capacity of 3 soil layers and specify a different set of displacement probabilities for each layer.
3. Module for optimizing the particles migration parameters according to the actual distribution. Using this module, the researcher specifies the actual distribution of the particles in the soil profile. The program specifies the probability values using the Monte Carlo method and gives preference to the options where $\Sigma(x_{i(\mathrm{act})} - x_{i(\mathrm{mod})})^2$ is the smallest. During a number of iterations, the program selects a set of

probabilities in order that the distribution resulting from the virtual experiment corresponds in the best way to the specified natural distribution.

The model studies have showed that, depending on the selected displacement probability, the pattern of particles distribution in the soil profile after a specified period of time can vary significantly. Specifying a different set of probabilities for different soil layers, we can obtain a «layered» distribution that is typical for alluvial floodplain soil or a depth ward monotonic decrease in the content of radionuclides that is typical for arid automorphic soils. It is reasonable to use simulation modeling with cellular automata method for solving some tasks related to the study of local circulation of radionuclides, dynamics regularities of vertical migration and distribution of radionuclides in the soil profile. The examples of distribution are shown in the Fig. 3e. Using this module for optimizing the parameters of particles migration, the researcher can specify the actual distribution of the radionuclides in the soil profile? During a number of iterations the program selects a set of probabilities in order that the distribution resulting from the virtual experiment corresponds in the best way to the specified natural distribution. Figure 3f shows the results of modeling the actual distribution of ^{90}Sr in the gray forest soil using the module for optimizing. In our opinion, the module for optimizing allows us to select the values of probability of displacement for specified vectors for homogeneous soil or a particular homogeneous layer with a high accuracy.

4 Conclusion

1. In natural forest and meadow soils of Transurals, the lower litter part and the upper soil layer (0–5 cm) are most contaminated with ^{90}Sr and ^{137}Cs. The contamination of different soils with radionuclides at the level deeper than 20 cm is slightly differed.
2. In floodplain bog soils, ^{90}Sr is distributed in the whole profile, and ^{137}Cs and ^{239,240}Pu are concentrated at a depth of 20–40 cm.
3. In floodplain meadow Soddy soils, ^{90}Sr is concentrated on a depth of 40 cm, and ^{137}Cs and ^{239,240}Pu remain mainly in the upper 0- to 10-cm layer.
4. In experiment with the decomposition of plant litter the pollution levels and the distribution of ^{90}Sr in the profile of laboratory soil were similar to the distribution in the natural soil, and the levels of contamination of laboratory soil with ^{37}Cs were approximately tenfold lower.
5. We have developed a computer program to simulate the transfer of radionuclides in the soil.

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