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Radioactive Contamination of the Soil: Assessments of Pollutants Mobility with Implication to Remediation Strategies

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Additional information is available at the end of the chapter

Abstract

Accidental releases, nuclear weapons testing, and inadequate practices of radioactive waste disposal are the principal human activities responsible for radioactive contamination as a new and global form of soil degradation. Understanding the radionuclide distribution, mobility and bioavailability, as well as the changes caused by the variation of environmental conditions, is essential for soil rehabilitation. This chapter aims to highlight the importance of evaluating radionuclide distribution, for the selection of proper *in situ* or *ex situ* remediation strategy. Attention was focused onto remediation methods based on radioactive pollutants redistribution, for enhanced separation (chemical extraction) or containment (*in situ* immobilization). When the excavation and off-site leaching treatments are uneconomic, impractical, or unnecessary, *in situ* stabilization by the addition of appropriate reactive materials is an alternative approach. The optimization of factors in control of chemical leaching methods, selection of cost-effective immobilization agents, especially among suitable wastes and by-products, and verification of long-term effects of remediating actions are the major challenges for future investigation in this field. Furthermore, the improvement and standardization of the methods for radionuclide speciation are necessary to enable comparison between studies and monitoring of the effects achieved by the soil treatments.

Keywords: radioactive pollutants, mobility, soil remediation, extraction, immobilization

1. Introduction

Radioactivity is a phenomenon related to unstable atomic nuclei with excess of energy and/or mass, which spontaneously decompose emitting ionizing radiation in the form of electromagnetic waves (gamma rays) or streams of subatomic (alpha, beta, or neutron) particles [1]. The activity of a particular radioactive substance is characterized by the constant decay rate and the half-life ($t_{1/2}$—time taken for the activity of a given quantity of a radioactive substance to decay to half of its initial value), and it is a general rule of thumb that ten half-lives are required for each radioisotope to be eliminated [2]. Since the half-lives of various nuclei vary from seconds to billions of years [3], the time required for their total decay significantly differ as well.

Some radionuclides occur naturally in the environment, and their presence is either cosmogenic or terrestrial. The ^{3}H, ^{7,10}Be, ^{14}C, ^{26}Al, and ^{39}Ar are the main radionuclides produced after the interaction of atmospheric gases with cosmic rays. On the other hand, the rocks, minerals, and consequently the soil, contain naturally occurring radioactive materials (NORM), characterized by a long half-life periods [3]. The most important terrestrial radionuclides are ^{238}U and ^{232}Th decay series, as well as ^{40}K. The world average values for soil activity coming from ^{226}Ra, ^{232}Th, and ^{40}K are 32 Bq/kg, 45 Bq/kg, and 420 Bq/kg, respectively [4].

The term radioactive contamination indicates the unintended or undesirable presence of radioactive substances on the surfaces or within solids, liquids, gases, or biota [5]. The origin of NORM is related to the formation of the planet; thus, their presence cannot be referred to as contamination. On the other hand, anthropogenic activities, related to the development of nuclear energy and its versatile use, have become important source of pollution. Since the middle of the last century, the radioactive contamination have appeared through the discharge of man-made radionuclides, making the ionizing radiation one of the important ecological factors, in line with other types of soil degradation (physical, chemical, and biological) [6]. Even though the radioactive contamination of the environment is relatively rare, it requires a great attention because of extreme degrading effects of ionizing radiation on living tissues. The adverse effects are in correlation with the quantity of absorbed energy, the penetrating power of the radiation, the duration of the exposure, as well as with the reproduction rate of the cells of a certain tissue [3].

In terrestrial ecosystems, soil corresponds to the major receiving pool of emitted radionuclides. Given that the nutrient cycles and the flow of energy present links between the abiotic and biotic components of the ecosystem, soils contaminated with radionuclides lose their ability to produce good quality agricultural crops and thus can be classified as degraded [6]. The issues related to the degradation of radioactively contaminated soils are being considered as an exceptional type of chemical contamination, with the additional, specific features related to the ionizing radiation.

The transport and fate of radionuclides in the soil are governed by a number of factors and the effects of their interactions; therefore, the detection and comprehension of the retention mechanisms are of great importance for the selection, development, and application of appropriate remediation technologies. In this chapter, the following topics were summarized

and discussed: (i) sources of soil contamination by radioactive pollutants, (ii) interactions with soils constituents, (iii) factors influencing radionuclide mobility in the soil (iv) methods for the assessment of radionuclide mobility in the soil, and (v) the remediation strategies based on the increase or decrease of pollutant mobility.

2. The key sources of soil contamination by radioactive pollutants

Contamination of the soil with the radioactive pollutants is an important origin of hazard for the environmental and health safety, as well as for the economy. Exploitation of the nuclear energy is a key source of pollution. Radiation can enter and affect the environment at any of the stages of the nuclear fuel cycle, starting with the excavation and processing of uranium ore, over production and recycling of the nuclear fuels, to the processing and disposal of radioactive wastes. The average uranium concentration in the earth crust is 2.8 mg/kg [7]. This radionuclide is contained with variable concentrations in the range of oxide, silicate, arsenate, vanadate, and phosphate minerals. Ores, processed by conventional uranium production methods, vary from reach (>20%, Canada) to very poor (0.01%, Namibia) [8]. Uranium is extracted from the ore matrix by hydrometallurgical process, and the final product, (the so-called yellowcake), used in the following steps of the nuclear fuel production typically contain 75–85% U_3O_8. Studies of the effect of uranium production process onto environmental pollution and the potential health risks have revealed elevated activities at cites around ore processing facilities and around old mines, in particular [9, 10]. Nowadays, almost half of world-wide uranium mining, and most of the mining in the USA, Kazakhstan, and Uzbekistan, was conducted by *in situ* recovery (ISR) method [11]. This process is based on uranium leaching from the ore matrix, within the deposit. ISR is the most economically efficient method of uranium extraction; however, the associated risks include contamination of drinking-water aquifer with uranium or other heavy metals [12]. At present, approximately 60.000 tonnes of uranium ore are mined annually to supply fuel for more than 430 nuclear reactors around the world, which provide approximately one-eighth of the world's electricity [11].

Any material that is radioactive itself or is contaminated by radioactivity at levels greater than the quantities established by the competent authorities, and which cannot be of further use, is characterized as—radioactive waste. Within civil society, this kind of waste arises mainly from nuclear power production, but also from a variety of industries, medicine, agriculture, research, and education and other activities in which radioisotopes are used [13]. The radioactive wastes are being classified based on the level of radioactivity (low, medium, and high) and the half-lives of the isotopes with predominant activity [14]. In the short-lived waste, predominant activity is defined by radionuclides with $t_{1/2} < 30$ years, whereas the long-lived wastes are characterized by isotopes with $t_{1/2} > 30$ years.

Processing of radioactive waste may result in an accidental release of the radionuclides during characterization, segregation, transportation, treatment, and disposal. By the review of the inventory of fission products important in the case of accidental releases, it can be concluded that ^{89}Sr, $^{90}Sr/^{90}Y$, ^{91}Sr, ^{92}Sr, ^{95}Zr, ^{97}Zr, $^{103}Ru/^{103m}Rh$, ^{105}Rh, $^{129m}Te/^{l29}Te$, $^{131m}Te/^{131}Te$, ^{132}Te, $^{131-135}J$, $^{140}Ba/$

[140]La, [134]Ce, [144]Ce/[144]Pr are important pollutants at the reactor stage; ^{90}Sr, [125m]Te/[129]Te, ^{131}I, [134]Cs, ^{137}Cs may be released during fuel element transport; ^{90}Sr, [95]Zr/[95]Nb, [106]Ru, ^{131}I, ^{137}Cs, [144]Ce/[144]Pr, and actinides are important at the fuel reprocessing stage; ^{90}Sr, [106]Ru, ^{137}Cs, and [144]Ce/[144]Pr contamination may occur during fission product solidification, whereas leaching from the final disposal may result in soil contamination with ^{90}Sr, ^{137}Cs, and actinides [15]. In addition to fission products, several corrosion products may become significant soil pollutants. Namely, during nuclear reactor operation, most metallic surfaces oxidize and form a layer of corrosion film rich in oxides of structural elements. This layer is exposed to high pressures and temperatures, where radionuclides are generated under the neutron activation [16]. Depending on the composition of the reactor materials and their trace elements, reactor type and design, thermal power, years of irradiation and shutdown period, the corrosion products and their relative proportions are different. The products of steel corrosion are [55]Fe, [59]Ni, [63]Ni, [94]Nb, ^{60}Co, [39]Ar, [54]Mn, with the ^{60}Co and [55]Fe being the most important in the first 10 years following the closure of a reactor, and [63]Ni, [94]Nb, [108]Ag in the next 50 years. Reinforced concrete's corrosion products are ^{3}H, ^{14}C, [41]Ca, [55]Fe, ^{60}Co, [152,154]Eu, whereas ^{3}H, ^{14}C, [152,154]Eu originates from graphite. Considering these two groups of materials, ^{3}H becomes the most prominent after 10 years, and ^{14}C, [41]Ca, [152,154]Eu after 50 years from the reactor shut-down. Taking into account both fission and corrosion products, 10–20 years after the reactor shutdown the most abundant radionuclides in contamination residues generally include ^{3}H, ^{60}Co, [55]Fe, and ^{137}Cs, whereas in the period 20–30 years, [63]Ni, ^{137}Cs, ^{60}Co, and ^{90}Sr generally prevail [16].

Another key source of soil contamination with radionuclides is nuclear weapons tests, particularly atmospheric, which have started in 1945 in the USA [17]. In the period 1945–1980, the power of USA atmospheric tests (428 megatons) was approximately equivalent of the size of 29,000 Hiroshima bombs [17]. Finally, in 1990, thanks to the moratorium signed by SSSR, UK and USA, nuclear testing was stopped. Atmospheric detonations produce radioactive debris of different particle size, which are partitioned in the tropo- and stratosphere and my precipitate over a period of a few minutes to 1 year, or longer [18]. The concern is especially focused onto released Pu isotopes, due to the high biological toxicity and long half-lives of its relevant isotopes (e.g., 24.2×10^3, 373×10^3, 81×10^6 years, respectively, for [239]Pu, [242]Pu, and [244]Pu) [19]. Furthermore, ^{137}Cs, ^{90}Sr, [241]Am, and ^{131}I are the released radioactive isotopes with major impact on the environment and irradiation of the human body [20]. The mentioned isotopes were predominantly found in most of the nuclear test sites worldwide, especially in western US soil [21, 22].

Nuclear accident are the events that led to significant consequences to people, the environment or the facility, such as the ones in Chernobyl (Ukraine, 1986) and Fukushima (Japan, 2011). These two events caused global contamination of the environment, including air, water, soil, and living organisms. Huge amounts of radioactive elements especially ^{131}I, ^{137}Cs, ^{90}Sr and the sum activity of [239]Pu and [240]Pu were dispersed into environment [23]. Some 40% of Europe has been exposed to Chernobyl's ^{137}Cs at a level 4–40 kBq/m^2 [24]. The size of the disaster can be illustrated by the fact that the maximum radioactive contamination in the soil in the 1993 was found to be 3500 times higher than the level before Chernobyl accident.

Apart from uranium mining and related fuel cycle activities, the industrial sectors which generate technologically enhanced naturally occurring radioactive materials (TENORM) include the following: mining and combustion of coal, the oil and gas production, metal mining and smelting, production of mineral sands (rare earth minerals, titanium, and zirconium), phosphate fertilizer industry, building industry, and recycling [25–27]. The dose of radiation coming from primordial radionuclides (^{40}K, ^{232}Th, ^{235}U, ^{238}U, and the members of decay series), which are normally found in natural minerals and ores (uranium ore, coal, phosphate rock, monazite, bauxite, etc.), can be elevated in their by-products and wastes such as phosphogypsum, fly ash, and red mud. Consequently, the releases from non-nuclear industries represent a continuous source of soil contamination with natural radioactive elements, by spreading of dust from rock and solid wastes dump, as well as by the overflow of wastewater from treatment ponds. Furthermore, years of application of phosphate fertilizers enriched with TENORM may become a source of soil contamination. Depending on the contamination level, restriction of land use or the remediation measures may be necessary. Finally, soil contamination may also arise from less common sources such as incidents during use of radioisotopes in medicine, industry, and agriculture [28].

At 160 U.S. Department of Energy (DOE) sites with radioactive contamination, ^{137}Cs, ^{226}Ra, ^{238}U, $^{238-242}$Pu, ^{60}Co, ^{232}Th, and ^{90}Sr were detected as the key artificial and natural radionuclides [29].

3. The interactions of radioactive contaminants with soil matrix and the methods of their identification

3.1. The nature of radionuclide interactions with soil components

Interactions of contaminants with soil matrix, and their variation with environmental parameters, are essential for radionuclide transport and fate, as well as for the risks to the living organisms and the environment. The uptake of radionuclides by soil can occur through diverse modes of interactions, while at the same time, other mechanisms are responsible for their elimination from the soil matrix (**Figure 1**). Due to the dynamic nature, heterogeneity and the overall complexity of the soil as a system, studying, understanding, and predicting the radionuclides behavior are the major challenges.

Factors influencing radionuclide distribution in the soil include the source term and the release conditions, transport and dispersion mechanisms, and the properties of the ecosystem [30]. Source term (ions, colloids, particles, oxidation states, etc.) influences mobility properties of radionuclides, since the transfer of mobile species in the ecosystem is faster in respect to the transfer of particles. Furthermore, the properties of the particular radionuclide, its chemical form and the reactivity, control the nature of its retention in the soil and the affinity to certain soil constituents.

Soil properties are primarily grouped into physical (texture, structure, porosity, water, air, and heat regimen), chemical (chemical and mineralogical composition, pH, microelements, micronutrients, salinity (EC), cation exchange capacity (CEC), organic matter, etc.) and bio-

logical (macroflora, macrofauna (rodents, insects, woodlice, mite, snails, millipedes, spiders, worms), microflora (bacteria, actinomycetes, fungi, and algae), and microfauna (nematodes and the protozoa)) [31, 32]. All five basic components of the soil, that is, minerals, water, organic matter, gasses, and the microorganisms, affect the binding and retention of the pollutants to a greater or lesser extent, depending on the pollutant type.
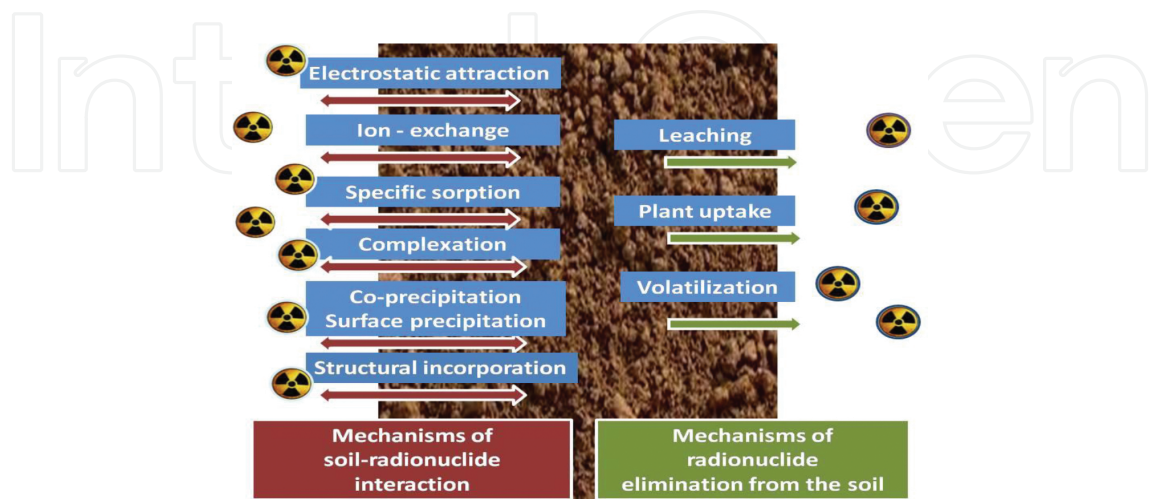

Figure 1. The mechanisms of radionuclide binding and elimination from soil matrix.

The interactions between radionuclide and the soil include physical (reversible) sorption governed by the uncompensated charges on the surface of the soil particles, and the chemical (principally irreversible) sorption through high affinity, specific interactions, and establishment of covalent bonds [33, 34]. The primary minerals in soil, mainly quarts and feldspar, are derived from the parent rock and make up most of the sand and silt fraction. Due to the relatively low specific surface area, their role in contaminant interaction is the smallest, and the attachment occurs through reversible sorption [35]. Secondary minerals, such as clay, result from physical, chemical, and biological weathering processes. Because of the unbalanced charges of structural ions, they are the carriers of permanent surface charge, which in combination with small particle size and large specific surface area make them important matrices for contaminant retention. Furthermore, oxides and (oxy)hydroxides of Fe and Al are abundant in amorphous form, with pH-dependent surface charge. Soil organic matter consists of chains of carbon atoms, containing polar and/or ionized surface functional groups, such as OH– and COOH–. Consequently, clay minerals, Fe, Al-oxides, and organic matter undergo a variety of interactions with contaminants.

3.2. Assessment of the radionuclide mobility in the soil

The bonds established between the particular radionuclide and the particular soil type can be assessed by different analytical approaches. Chemical reagents of various composition, strength, and selectivity are the most widely used, in the single stage or sequential extraction protocols [30, 36–41]. The aim of such tests was assessment of the transport mechanism in a soil profile and the potential toxicity, with implications to the risks to the biota and the ground

water reservoirs. In general, weaker bonds between the pollutant and the soil components signify higher mobility of radionuclide, its increased possibility to reach the plants and soil organisms and to enter into the food chain. However, the mobility and bioavailability of closely related, they cannot be equalized in the interpretation. Bioavailability processes are defined as the physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments, they incorporate a number of steps and represent the amount of a contaminant that is absorbed following skin contact, ingestion, or inhalation [42]. On the other hand, the bioaccessibility of the contaminant is defined as its fraction soluble in the gastrointestinal tract and available for absorption.

Review of the literature shows that a wide spectrum of single-stage extraction methods for soil analysis is in use [36, 42]. Basic groups of reagents include acids, chelating agents, and salts; moreover, reagent concentrations and other experimental conditions are considerably different (**Table 1**). In contrast to the well-established methods for the determination of soil major nutrients and fertility, the procedures for the extraction of pollutants are not standardized.

The most common chemical reagents		Common concentration ranges (mol/L)
Acidic solutions	HNO_3, HCl, CH_3COOH, H_2SO_4	0.01–2
Chelating agents	EDTA*, DTPA**	0.005–0.01
Salt solutions	$CaCl_2$, $NaNO_3$, NH_4NO_3, $AlCl_3$, $BaCl_2$	0.01–0.1
Buffered salt solutions	NH_4CH_3COO/CH_3COOH (pH 4.8, pH 7)	1

*Ethylenediaminetetraacetic acid;
**Diethylenetriaminepentaacetic acid.

Table 1. The common leaching solutions in single stage soil extraction analysis [36, 42].

In addition to acidic and salt-containing solutions, the chelating agents are applied, due to their efficiency in extracting potentially bioavailable soluble complexes of radionuclides with organic matter. The results of leaching tests represent a rough measure of mobility, as the actual mobility in the field depends also on moisture, leaching, root uptake of nutrients, activity of microorganism, and many additional factors. Furthermore, the agreement between chemically extracted and fractions available to biota should be confirmed empirically, for wide variety of contaminated samples [43].

Speciation analysis is conducted for the identification and determination of the different chemical and physical forms of elements in the soil matrix [44]. The distribution of radionuclides is related to their affinity towards certain soil components; thus, they can exist as a free ions or in the form of soluble complex ions in interstitial solution; as exchangeable ions attached to the soil surface, they can be associated with soil organic fractions, occluded, or co-precipitated with metal oxides, carbonates, phosphates, or other secondary minerals, and incorporated inside the crystal lattices of primary minerals.

The sequential extraction protocols were primarily developed for the determination of the distribution of stable macro- and micro-constituents of the soil. Identification of the mobility and availability of trace elements, both the essential ones and the pollutants, is particularly important for the improvement and protection of the plant development and growth, and for the health of the ecosystem as a whole. Different sequential extraction methods have been proposed to separate the fractions of elements from various pools. The so-called Tessier method [44] and the method proposed by the European Community Bureau of Reference—the BCR method [45], are the two commonly used protocols, while many others are based on their modifications. Additionally, a modified version of Tessier's method was proposed at the Speciation Workshop organized by the National Institute of Standards and Technology (NIST), in order to optimize the protocol of soil extraction and select operationally defined fractions which can be separated by appropriate chemical reagents [46].

Evaluation of element distribution in soils by the sequential extraction is based on the assumption that mobility decrease with each extraction step (**Figure 2**), implying that under natural conditions elements in water soluble and exchangeable fractions are the most mobile and bioavailable, whereas those in residual fractions are the most tightly bound.
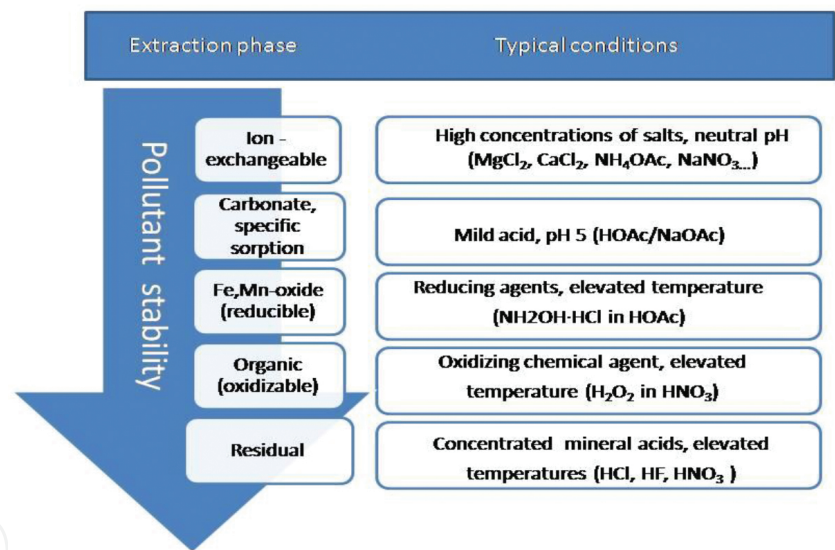

Figure 2. Common phases in sequential extractions based on Tessier's protocol [44].

The lack of the standardized procedure for the determination of pollutant mobility makes the interpretation and the comparability of the results difficult. In addition, the effect of the reagents may be questionable. For example, extracting solution having pH 5, used for the dissolution of carbonate phase, may also sequester ions specifically sorbed onto surface of other soil constituents [47]. The fractions of pollutants are defined only operationally; thus, instead of being associated with the terms *mobility* and *bioavailability*, they should actually be related to the extracting solution or the applied protocol [48]. Nevertheless, in the scientific and the technical literature, free ions, water-soluble complexes of radionuclides and the species associated by reversible, physical sorption, are commonly considered as the *mobile fraction* [49].

On the other hand, the term *inert species* refers to fraction of colloids and particles deposited in soils, together with the fraction of radionuclides irreversibly bound to or incorporated into the mineral lattices. The results of sequential extractions can be used for the calculation if the mobility factors of radionuclides (MF) [49]:

$$MF = \frac{\text{Mobile species} (\text{Bqm}^{-2})}{\text{Total deposition} (\text{Bqm}^{-2})} \times 100 (\%)$$

(1)

where the mobile species include the fraction such as H_2O and CH_3COONH_4 extractable and that taken up by vegetation from the same site.

Although none of the methods can provide the absolute quantities associated to the specific component of the soil, such analyses represent valuable tool in elements mobility and availability assessment, and for tracking the effectiveness of soil remediation actions. Experiences achieved by practicing single and sequential chemical extractions reveal advantages of these methods but also a need for further research and developments due to increasing soil contamination which requires fast, reliable, and cost-effective assessment.

In addition to extraction methods, studies of the radionuclide retention mechanism can be complemented by the determination of the type of the surface complexes, identification of the radionuclide incorporation in the crystal lattice of existing minerals, or the formation of new solid phases, etc., for which instrumental techniques are applied (X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), scanning electron microscopy with energy dispersive X-ray spectroscopy (*SEM/EDS*), etc.) [50, 51].

Furthermore, bioassay tests involving plants, animals, and microorganisms, are valuable for the analysis of radionuclide mobility and bioavailability [52]. Soil-to-plant transfer factors (TF) have been widely used in radioecology, in order to quantify the availability of soil radionuclides for plant uptake [36]:

$$TF = \frac{\text{Plant activity concentration} (\text{Bq kg}^{-1})}{\text{Total soil activity concentration} (\text{Bq kg}^{-1})}$$

(2)

As soil-to-plant transfer considerably differs between different plant species and the seasons, this method also gives crude estimations of potential radionuclide bioavailability. In spite of limitations, transfer factors are currently accepted as the most practical way of describing plant uptake. Also, several in vitro methods have been developed for the prediction of the relative bioavailablity of the contaminants, using physiologically based fractionation schemes [42, 53]. These methodologies mimic key processes that take place in vivo, such as contaminant dissolution, and after establishing a strong correlation between the in vivo and in vitro results, these methods have a potential to overcome the time and expense limitations of in vivo studies.

3.3. Factors influencing radionuclide mobility in the soil

A capacity of the soil itself to immobilize radionuclide is the main factor controlling activity concentrations available to biota, and it operates in conjunction with the numerous external factors. Soil texture and structure, mineral composition, organic components, redox potential (Eh) and pH, as well as rainfall, climate changes, and soil management, are recognized as important for radionuclide mobility [54]. The pH of the soil, cation exchange capacity (CEC), and total organic carbon (TOC) are the physicochemical characteristic most often correlated with the distribution of the radionuclides [40]. Alkaline soils are characterized by the presence of carbonates and have a high saturation of base cations (K^+, Ca^{2+}, Mg^{2+}, and Na^+), whereas acidity in soils comes from H^+ and Al^{3+} ions in the soil solution and sorbed to soil surfaces. The surface charge of minerals is a major contributor to soils CEC and influences the soil's ability to retain important nutrients and the pollutants. The texture of a soil is based on the relative content of sand (0.05–2.00 mm), silt (0.002–0.05 mm), and clay (<0.002 mm) fraction. Due to the finest granulation, clays minerals exhibit the largest surface area, important for soil chemistry and CEC, but also for water-holding capacity important for transporting nutrients and pollutants to soil organisms and plants. In addition, soil organic matter significantly contributes to the soil CEC and to the water-holding capacity.

Based on the literature data, the influence of soil properties and other condition on the mobility of some important pollutants is given in **Table 2**.

	Radionuclide			
	Cs	**Sr, Ra**	**U, Pu**	**I**
Chemical form	Cs^+	Sr^{2+}	PuO_2^{2+}, $Pu(NO_3)^{3+}$	I_2, I^-, IO_3^-, CH_3I
			Mobility	
pH decrease	Increase	Increase	Increase	
Clay content decrease	Increase	Increase	Increase	
Sand content decrease	Decrease	Decrease	Decrease	Increase
Humus content low	Not clear	Decrease	Decrease	
CEC decrease	Increase	Increase	Increase	
Aging	Decrease	Weak effect	Decrease	

Table 2. The effect of soil physicochemical properties and aging on the mobility of radionuclides [55, 56].

Apart from soil type, different sources of variability may influence the fractionation patterns and cause the shift from less available to more available fractions, or vice versa. Generally, the increase of contaminant concentration not only increases the overall activity in the soil but also leads to redistribution from the less to the more available fractions [57]. Radioactive contamination introduces new elements into the ecosystem and, in distinction from the transport of stable elements and NORM, transfer of contaminants through the trophic chains occurs under non-equilibrium conditions. Consequently, ageing affects a decrease in the chemical mobility

and biological availability of most of the radioactive pollutants [58]. The ageing process actually involves a set of reactions related to the enhancement of radionuclide sorption and fixation by the soil solid phase (i.e., the precipitation or penetration into the crystalline lattices of different mineral constituents. Aging exhibits a different effect on different ions. Increased contact times (months to years) were found to affect gradual reduction of Co^{2+} ions mobility [57, 59]. Time-dependent studies on the variation in Cs^+ bioavailability have revealed that over years, a decrease in the labile fraction of ^{137}Cs in soils was correlated with a decrease in soil-to-plant transfer [60]. In contrast, due to low sorption affinity of ^{90}Sr towards soil constituents, impact of aging is very weak considering ^{90}Sr speciation [40]. The behavior of Sr^{2+} and its uptake by living organisms are controlled by its similarity to calcium; thus, regardless of the soil type, contamination level, and aging time, it was largely found in water-soluble and ion-exchangeable fractions of soil. Seasonal effects may also cause variations in radionuclide mobility, and these effects can be controlled by appropriate sampling plan [57].

4. Increase/decrease of radionuclide mobility as essential soil remediation strategy

As the environmental conditions change, the distribution of pollutant also changes, causing the increase or the decrease in mobility. Knowledge of such dependencies represents the theoretical background for the development of mobilization/immobilization remediation methods. Furthermore, exploration and development of suitable solid and liquid media are fundamental in support of these technologies. Mobilization techniques imply weakening of bonds with the soil constituents provoking desorption, dissolution, and chalation of the pollutant [61, 62]. On the other hand, the general idea of the radionuclide immobilization (stabilization) is to induce chemical reactions, precipitation, and other processes which cause redistribution of the contaminants from more labile to more stable forms [61, 63]. Both principles exhibit certain benefits and drawbacks. Stabilization techniques are usually less expensive and easier to perform in comparison with the alternative processes; however, the total activity concentrations remain in the soil, posing a constraint for the future uses. Otherwise, the techniques based on the pollutant exclusion from the soil matrix represent a permanent solution for the contaminated site. However, transportation, consumption of the chemicals and the energy, and further management of the resulting liquid phase with the extracted pollutants, make these techniques complicated and costly. Remediation activities may also result in some negative effects on the soil properties, including fertility; thus, evaluation of suitable strategies and decision-making process require detailed knowledge of all these aspects.

4.1. Extraction of radioactive contaminants from the soil matrix

Chemical extraction is the technique that stimulates the redistribution of contaminants from the solid phase to the solution, in order to selectively remove the contamination, or to enhance its physical separation [61, 64]. The contaminated soil is excavated and treated off-site. After

the treatment, the soil is returned to its original location, while the activity remains concentrated in the extraction medium. The extract is subsequently treated to precipitate the activity and return the leaching reagents to the process. Otherwise, the extracting solutions can be implemented *in situ*, to increase the radionuclide mobility in the soil and enhance their subsequent uptake by plants (combination with phytoextraction) [65].

Radionuclides in the soil can be re-mobilized by four principal means [66]: (1) changes in the acidity, (2) changes in the ionic strength of the solution, (3) changes in the soil redox potential, and (4) formation of soluble complexes. To extract the pollutants, acids operate on the ion-exchange principle, and by dissolution of soluble soil components. Highly concentrated solutions of inorganic salts displace the radionuclides from ion-exchangeable sites by mass action, and if implemented at low pH this effect is combined with the effects of acid leaching. Chelating agents solubilize metals through complexation, while redox manipulation aims to enhance solubilization by the change of valence and thus chemical properties. The most common chemical agents are inorganic salts ($CaCl_2$, NaCl), mineral acids (HCl, H_2SO4, HNO_3), and complexing agents (EDTA, DTPA, oxalate, citrate, etc.) [61, 65, 67].

Selection of the proper chemical extracting reagent is influenced primarily by the radionuclide type, its speciation pattern and the characteristics of the soil. Pollutants that are majorly accumulated in ion-exchangeable, carbonate, and Fe, Mn oxide fractions are the most suited for the removal by chemical leaching [68]. The soils characterized by low pH, low content of clay, and humic substances are the promising candidates for such treatments [61].

In order to extract the target metal from the soil environment, the strength of the radionuclide-chelating agent complex must overcome the strength of the bonds keeping raionuclide attached to the soil surface. The efficiency of EDTA is superior, and it is usually applied at pH 4–8, as the EDTA-complexes can be re-adsorbed on soil surface sites at lower pH [69]. In addition to the high price, selectivity of EDTA towards target radionuclides, its recovery and reuse are the major drawbacks. Furthermore, its low degradability can be a persistent problem after the soil treatment. Thus provided that they enable efficient removals of pollutants, and acidic and salt-containing solutions are more acceptable due to lower environmental impact and the ease of regeneration.

In the comprehensive investigation of appropriate chelating agent for the extraction of various radionuclides, the regressive empirical predictive model was developed as a selection tool [62]. Using as the input variables, the properties of the chelators, various stability constants, radionuclide distribution, and the soil properties (mineralogical composition, pH, clay content, CEC, etc.), the following adequate chelator for target radionuclide were proposed: EDTA, DTPA, and nitrilotris(methylene)triphosphonic acid (NTTA) for Ba and Ra; 2-aminoethanethiol, EDTA, DTPA, thiobis(ethylenenitrilo)tetraaceticacid (TEDTA), and N-2-acetamidoiminodiacedicacid (ADA) for Pb and Th; whereas iminodiaceticacid (IDA), nitrilo-triaceticacid (NTA), and ethylenediiminodiacetic acid (EDDA) were suggested for the extra-ction of Pu and U.

Selective removal of ^{137}Cs and ^{90}Sr from soil poses a problem, due to the lack of suitable complexing agents [61]. Although certain crown ethers form complexes with these cations,

due to the toxicity and high cost of such agents, large-scale agricultural applications are impractical. Solutions of HCl, $CaCl_2$, EDTA, tartaric, and citric acid, with different concentrations of reagents, were applied to soil artificially contaminated with Sr^{2+} and Co^{2+} ions [39]. Due to its predominant association with ion-exchangeable fraction, Sr^{2+} ions were efficiently desorbed using Ca^{2+} or acidic solutions. On the other hand, Co^{2+}, which was largely distributed between carbonate and Fe, Mn-oxide fractions, was leached most efficiently by complexing agents.

Chemical extraction processes have a large potential in the rehabilitation of the soil that have undergone radioactive contamination and their effectiveness can be additionally improved by optimizing reagent type and concentration, soil/solution ratio, pH, contact time, mixing, and other factors.

4.2. Radionuclide immobilization (stabilization) by soil amendments

Despite the fact that the main objective of the soil remediation was the removal of the maximum amount of pollution, the major obstacles for the routine application of such an approach are the processing and the disposal of the radioactive waste resulting from the soil clean-up [70]. The insufficient storage capacities, especially for waste classified as low level, long-lived, are significant and global problem. As a consequence, immobilization treatments are being rapidly developed, with main goals to reduce the risk of exposure and uptake by biota, and the risk of the spread of contamination.

The application of soil amendments is performed on site (*in situ*) which makes such technologies fast, simple, and effective. Alternatively, soil amendments can be applied in *ex situ* process, where soil is firstly physically removed from the site, pretreated, mixed with a stabilizing amendment, and then returned to its original location [71].

As the most of the radionuclides in soil exist in the cationic form, increase in pH, clay content, and CEC lead to an increase in pollutant stability (**Table 2**). Consequently, water-soluble and water-insoluble amendments are applied, with a role to modify the environmental conditions in favor of radionuclide stabilization or to directly interact with the contaminants (or both).

In order to raise pH and lower pollutants accessibility to plants, the materials traditionally applied to soil are carbonates, lime, and phosphates [72]. Other soil amendments that are currently in use or are under consideration and verification have been modeled after stabilization or encapsulation agents (such as cement) used for safe disposal of radioactive and hazardous wastes. Various forms of aluminosilicates, phosphates, carbonates, silicates, oxides, and hydroxides were largely investigated [65, 72]. In general, solid matrices that have shown superior immobilization potential towards radioactive ions in aqueous solutions are suitable for testing in the contaminated soil. Based on the numerous investigations of the sorption affinities and capacities toward variety of radioactive pollutants, the most prominent groups of materials are aluminosilicates [73–80] and phosphates [81–89]. The main operating mechanisms are quite different for these two groups: while aluminosilicate addition to soil increases the number of sorption sites, phosphate materials, mainly from the apatite group, act through several removal mechanisms (ion-exchange, formation of specific surface complexes, and

structural incorporation of pollutants by co-precipitation and dissolution/precipitation processes).

Aluminosilicates, primarily clay minerals, and zeolites are inorganic ion-exchangers with high surface area, which have been conventionally used for water treatment processes, for the treatment of liquid nuclear waste, and for the protection against nuclear waste leaking [79–90]. Natural zeolites are the framework aluminosilicates, with variable porosity due to which they can selectively capture the ions having an appropriate radius. Zeolites are excellent sorbents of fission products that otherwise exhibit very low affinity for sorption on solid surfaces (such as Cs and Sr isotopes [78, 80]. Clay minerals (montmorillonite, vermiculite) are layered aluminosilicates, in which ion-exchange is typically associated with cations situated in clay mineral interlayers [72]. The stabilization of Cs^+ and Sr^{2+} contamination in the sandy soils was tested using different synthetic and natural zeolites [91]. With the addition rate of 1%, the maximum reduction of soil-to-plant transfer factor of 12.5 for Cs^+ and 24.5 for Sr^{2+}ions, was observed, as well as the significant changes in cationic composition and pH of the soil. By comparing the effect of various materials onto Sr^{2+} immobilization in the soil, zeolite has been identified as the most efficient, followed by bone char, synthetic hydroxyapatite, and phosphate rock [92]. The most of the results have been obtained on the laboratory level or out of small-scale field applications, while in solving the actual problems of soil contamination, applications are generally connected with Chernobyl and Fukushima disasters.

The other promising group of materials is the phosphate group. Among different soluble and sparingly soluble phosphate bearing materials, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) exhibited superior physicochemical and sorption properties, that is, low solubility in water, high specific surface area, high buffering capacity, and the high sorption capacities towards variety of cationic and anionic pollutants [93]. HAP is by far the most selective to U and Pb, due to the removal mechanism which involve dissolution of HAP and precipitation of thermodynamically more stable Pb and U containing phases [87, 94]. In soil, apatite matrices were highly effective for U uptake; however, the increase of organic matter content influenced the decrease of amendments efficiency [95]. Furthermore, the selectivity and capacity of HAP towards Pu, Co, Ni is very high, moderate for Sr, while low considering Cs and Tc [78, 81–84, 86–88].

Comparing different apatite forms (synthetic, mineral, and biogenic), the product extracted from fish bones exhibited the best sorption properties, due to CO_3^{2-} substitutions, low trace metal concentrations, poor crystallinity, and high microporosity necessary for optimal performance in the field [87]. Giving that this sorbent is produced from the commercial fish industry waste, it is both environmental friendly and cost-effective for large-scale operations. However, the bioavailability of essential trace elements was found to decrease at high HAP addition rates (5%), while uptake of As by plants was found to increase after HA treatment [96]. These results demonstrate that HAP application for the remediation of contaminated soil must be optimized and controlled.

In addition to animal bones as the source material for apatite production, many other industrial by-products, wastes, and recycled materials are being tested as potential soil additives [65, 72]. In order to preserve natural mineral resources and reduce the costs of the immobilization

treatments, application of such materials may represent a sustainable alternative. Another benefit comes from the reduction of the amount of accumulated wastes and their impact on the environment. Coal fly ash and bauxite residue (red mud) are mineral, oxide-based, residues, which exhibit high sorption potential for a range of radioactive pollutants [97–101].

Fly ash has a silt loam texture (<90% of the particles having a diameter of <0.010 mm), and it is composed mainly of aluminosilicate structures, quartz, mullite, hematite, magnetite, and calcite [102]. The pH values of fly ash vary in the wide range 4.5–12.0, depending on the content of sulfur in the parent coal. Fly ash was considered as an additive in agriculture, for improving soil properties [102], and also as an additive for stabilization of heavy metals in polluted soil, with the promising results [103–105].

Red mud is by product obtained after bauxite processing, which primarily consists of Fe, Al, Si, and Ti oxides and zeolite-like minerals [106]. Due to the nature of Al extraction process, this material exhibits extremely high pH (10–12), and it is high capacity sorbent especially for pollutants in cation form. Numerous laboratory, pot, and field studies were conducted in the past years regarding red mud utilization in remediation of heavy metal polluted soils, and its potentials (both as a liming additive, and as a sorbent) have been demonstrated [107]. However, radionuclides, as pollutants, have gained much less attention and the further research in this field is encouraged.

In general, there is a lack of the long-term studies on the overall effects of waste material additions on the soil properties. The variation in the composition of waste material and by-products adds uncertainty to their performance, and moreover, leaching of potentially hazardous substances from the waste material itself must be carefully evaluated. The activity levels of natural radinuclides can be elevated in fly ash and red mud with respect to parent coal and bauxite ore, therefore, a special attention should be paid to this aspect in order to keep activity levels in the permitted limits for soil.

5. Conclusion

The source term and a wide variety of soil and environmental parameters affect the radionuclide behavior in terrestrial systems. Weaker bonds between the pollutant and soil components implicate higher mobility of pollutant, higher potential to get into the solution and to be adopted by the biota. In addition to total concentration of the pollutant, understanding of its environmental behavior by determining distribution pattern in different fractions of the soil is of principal importance for the selection of optimal remediation technologies. Due to the large number of factors that affect the outcome of the soil rehabilitation process, selection of optimal solution must be done on a case-by-case basis. Still, some guiding principles can be derived from the research studies and the practical experience: pollutants mainly bonded in exchangeable, carbonate and reducible phase are suitable for chemical extraction, while removal of contaminants from organic and residual fraction is neither economical nor feasible. Optimization of extracting solution composition, pH, the time, and the mode of the interaction with the soil are the perspective fields of research which must include the type of the soil and

the radionuclide, and the effects of the extracting solution to other important soil characteristics. Analyzing the contamination level, the size and the properties of contaminated area, *in situ* soil immobilization may prove to be more suitable solution which permanently increases sorption capacity of the soil. The use of mineral-based amendments as soil remediation additives should be as much as possible substituted by appropriate waste materials and by-products, which environmental compatibility, selectivity, and long-term effectiveness, must be verified on a variety of soil types. Immobilization technologies may be particularly useful if applied in combination with conventional *ex situ* (soil removal, chemical extraction) or *in situ* technologies (bioremediation, phytoremediation, reactive barriers, capping, monitored natural attenuation), for the stabilization of the residual activity.

Acknowledgements

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