

Radionuclides and Heavy Metals in the Environment

Dharmendra K. Gupta
Clemens Walther *Editors*

Uranium in Plants and the Environment

Radionuclides and Heavy Metals in the Environment

Series Editor:

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Preface

Uranium (U) is the heaviest naturally occurring actinide, existing almost entirely as the primordial isotope ^{238}U (99.27%, half-life of 4.5 billion years), as ^{235}U in minor quantities (0.72%), and as ^{234}U in trace quantities (0.0055%). With an average concentration of 0.0003% (3 mgkg^{-1}) in the Earth's crust, uranium is present in all soils; in rocks such as volcanic rocks, granites, dark shales, sedimentary rocks that contain phosphate, and metamorphic rocks; and in seawater (3.3 ppb of U by weight ($3.3 \text{ }\mu\text{gkg}^{-1}$)). Uranium concentration in the Earth's crust may range from 1 to 4 mgkg^{-1} in sedimentary rocks to tens or even hundreds of mg/kg in phosphate-rich deposits or in U ore deposits. In surface soils and sediments and in aqueous systems, U reacts with oxygen to form predominantly the hexavalent uranyl ion (UO_2^{2+}) which is highly stable and soluble, which determines its mobility, bioavailability, uptake, and toxicity. Contamination of the biosphere by extensive release of uranium (or its progenies) poses serious threats to living organisms, due to chemical and radiological toxicity. Anthropogenic U contamination by mining and milling operations contributes to the degradation of the environment. Even before its formal discovery by the German chemist, Martin Klaproth, in 1789, U has been used for a wide variety of purposes for coloring glass and ceramics. Its actual use is dominated by the nuclear power industry, but also for military purposes.

Uranium has no essential biological function in the organisms, but a wide range of both terrestrial and aquatic organisms uptake U from the environment. For example, plants, bacteria, algae, and fungi were shown to accumulate U, and it has been reported that the biological action of bacteria, algae, fungi, and plants can affect U speciation and thus U bioavailability by adjusting the pH, extracellular binding, and transformation and formation of complexes or precipitates. These organisms can thus contribute in decreasing or increasing U entry into the food chain but could also be used to develop bioremediation tools to decontaminate uranium-polluted surroundings. In fresh water, numerous physico-/biochemical variables may affect U speciation, bioavailability, uptake, and toxicity, which include pH, hardness, natural organic matter, and microbial activity. In the case of soil, migration and mobility of radionuclide always depend on various factors including pH, texture, exchangeable

calcium/potassium, organic matter content, etc. and also weather conditions, plant species, and land-use practices.

Generally, plant roots are associated with microorganisms, and these links can have direct or indirect effects on the mobility, availability, and acquisition of elements by plants. The fast uptake of uranium by roots might result due to precipitation of U in the apoplasm as was shown for other heavy metals and also might be possible due to adsorption of U on the cell wall. Plant cell walls are made up of cellulose fibers, hemicellulose, pectin, and glycoproteins. It is well-known that the cell wall also works for root cation exchange capacity (CECR) basically for functional groups of polysaccharides, including carboxyl and galacturonic acid groups of roots, and, to a minor extent, for phenolic and amine groups. There are two ways for radionuclides to enter plants: either through the roots or through the stomata (direct deposition from the atmosphere). Stomatal entry is supposed to account only for a small fraction of total radionuclide uptake. When a radionuclide enters through the cuticle layer, it is dynamically transported inside the plant cells through a symplastic pathway and with an exchange mechanism between the phloem and the xylem.

The peculiarities of plant uptake and translocation of uranium are highly specific for different types of plants and soil. Soils high in phosphorous content may tend to suppress uranium uptake in plants. Mobility of U is reduced in finer-textured soils and those high in organic matter. Plants cannot differentiate isotopes of heavy elements and consequently take up isotopes in the ratios present in soil solution. The utmost forms of plant-available U in shallow groundwater are soluble carbonate complexes, with uranium dominantly present in the hexavalent oxidation state. Generally, the soil-to-plant relocation of elements is often parameterized by the transfer factor (TF). Basically, the TF is the activity concentration of the radionuclide per unit dry mass in the plants (Bq kg^{-1}) divided by the one in the soil (also given in Bq kg^{-1}).

During the past two to three decades, phytoremediation practices became a very attractive popular alternative to the conventional expensive and energy- and instrument-intensive, chemical-based restoration techniques of the vast polluted areas of land and water. Plants are usually resistant to moderate concentrations of radionuclides. Nevertheless, biosorption to cell walls, extracellular precipitation, reduced uptake, or amplified efflux are mutual tools from which plants check abiotic stress and also decrease the absorption of metal inflow in cells.

The most remarkable features of this book are interrelated to how U enters the ecosystem and its translocation from soil to plants and finally into the food chain of man. Chapters 1–3 deal with the beginning of the nuclear age till now, impact of U mining on human health, and soil-to-plant transfer of U and its distribution with a case study on Belarusian soil. Chapters 4 and 5 focus on biogeochemistry of U in tropical environment and mechanism of U accumulation in agricultural plants. Chapters 6–8 focus on what are the factors influencing soil-to-plant transfer, its translocation mechanism, its correlation with other metals, and uptake and phytoremediation approaches. Chapters 9–11 emphasize on the influence of U speciation on uptake mechanism, epidemiological studies with some modeling, legacy, and

risk assessment. The information collected in this volume will bring in profound knowledge of U uptake and translocation and its toxicity in plants and finally its effect on health.

Dr. Dharmendra K. Gupta and Prof. Clemens Walther individually thank all authors for contributing their valuable time, knowledge, and enthusiasm to bring this book into its present form.

Hannover, Germany

Dharmendra K. Gupta
Clemens Walther

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Uranium in the Beginning of the Nuclear Age: Reflections on the Historical Role of Jáchymov and an Overview of Early and Present Epidemiological Studies



Jozef Sabol

Abstract Following its discovery, more than 200 years ago, uranium found useful applications in a number of various areas especially those related to industry, research and also medicine. The uranium history has been closely associated with the discovery of radioactivity which opened the door to the separation and later to the production of many useful radionuclides. The importance of uranium was recognized particularly owing to its ability to undergo fission process leading to the release of much more energy than it is possible to acquire from chemical reactions. Namely, the fission has been widely utilized in nuclear reactors to generate electricity in nuclear power plants. Such reactors are also used to produce a great number of radionuclides and for fundamental and applied research. Unfortunately, the fission has also been used for military purpose that resulted later in the construction of weapons of mass destruction. The extensive demand for uranium led to the expansion of uranium mining, milling and processing which led to some problems including exposure of workers and the radioactive contamination of the environment. The health effects associated with uranium and its compounds were fully recognized only during the last 70 years. This resulted in worldwide adoption of the relevant strict measures for adequate protection of people and the environment in line with the latest international safety requirements. The data concerning these health effects were acquired from numerous epidemiological studies based on which relevant safety procedures have been developed and implemented. The chapter presents a short overview of the uranium's early history, which began in Jáchymov, together with uranium mining, uses and the assessment of its biological effects based on epidemiological studies.

Keywords Uranium · Mining and milling · Radioactivity · Radium · Radon · Decay products · Fission · Use of uranium · Nuclear fuel cycle · Health effects · Epidemiological studies · Radiation protection

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1 Introduction

Uranium belongs to the most important *naturally* occurring nuclides. It has a silvery-white colour and is about 70% heavier than lead. One of its isotopes, ^{235}U (uranium-235), is the only fissile element found on earth. The use of uranium to produce *nuclear energy*, for peaceful, but also for military purposes, has contributed substantially to changes in the life of mankind over the last 70 years. The huge energy released by the *fission* of uranium is associated with the splitting of its nucleus into two smaller fragments after this nucleus is struck by a neutron. The creation of these fragments is accompanied by the release of 2–3 neutrons which can then split other uranium nuclei present in their vicinity.

Uranium is more common than other metals on earth. It can be found in very low concentration in soil, rocks and water everywhere. There are several places in the world that have uranium concentrations large enough to be cost-effective to mine.

There are *three main isotopes* of uranium, namely, ^{238}U , ^{235}U and ^{234}U . The first two are considered primordial nuclides which existed on earth since the time it was formed. Their half-lives are sufficiently long so that they have survived to the present day. By far, the most abundant of uranium isotope is ^{238}U (99.27%), while the other isotopes are found in the earth's crust in much lower percentages, namely, ^{235}U (0.720%) and ^{234}U (0.005%). While ^{238}U and ^{235}U represent the parent isotopes of the respective *uranium decay chains*, the isotope ^{234}U is formed as one of the decay products formed within the ^{238}U series. This is illustrated in Fig. 1.

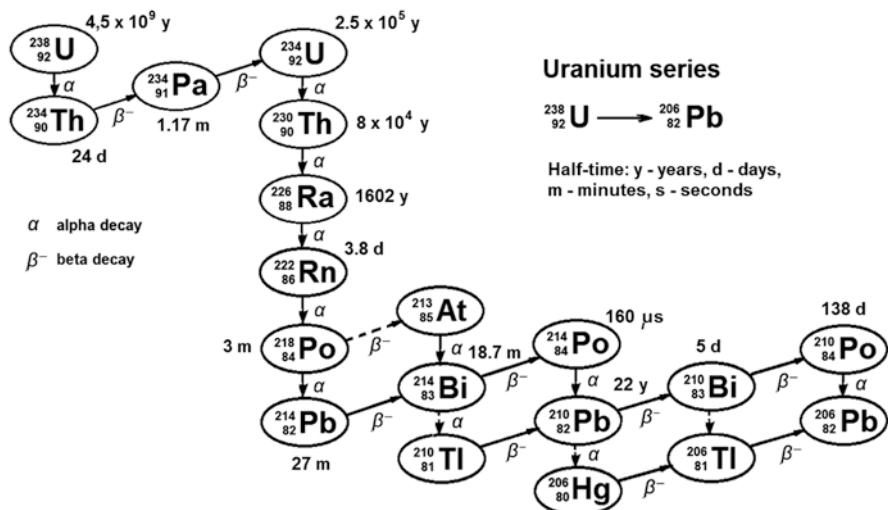


Fig. 1 The decay chain of ^{238}U illustrating the formation of all its essential elements which are finally decayed to form a stable nuclide of ^{206}Po . The decay of ^{234}Th , ^{234}Pa , ^{226}Ra , ^{214}Pb , ^{214}Bi and ^{210}Bi results not only in the emission of charged particles (α or β^-) but also in the release of the accompanying gamma photons

Another uranium series, the ^{235}U series, usually referred to as the actinium series, can be presented in a form like that in Fig. 1 or using a relevant table with some basic data (Table 1). In both series there are some prominent radionuclides, such as radium, polonium, radon and many others, which can be found in uranium ore and then extracted in a sufficiently pure form for suitable applications. One such example is radium which was widely used for the early treatment of cancer patients.

Up until now, science has recognized something like *21 different uranium isotopes*, most of them artificially engineered using nuclear reactions and chemical processes. Most of them have marginal practical significance; some are characterized by extremely short half-lives or are found on the earth only in trace concentrations.

The history of uranium began more than 200 years ago, from its discovery in 1789 by Martin H. Klaproth to recent years when uranium became one of the most vital elements, alone or in the form of its decay products. One may formally distinguish between the uranium eras up to 1896, when its *radioactivity was revealed*, through the second period up to the 1940s, when it was used in research, medicine, glass and ceramic industries as well as in radon spas. During the third period, uranium fission began to be utilized in nuclear reactors and, regrettably, also in nuclear bombs.

It took some time before reliable information was acquired relevant to the deleterious biological effects associated with the internal and external exposure to uranium and its decay products. After intensive medical and epidemiological studies as

Table 1 Radionuclides in the ^{235}U series which finally decay to the stable ^{207}Pb (After, Martin 2013; Morss et al. 2006; L'Annunziata 2003)

Nuclide		Decay (particles emitted)	Half-life
Symbol	Name		
^{235}U	Uranium	α	7.04×10^8 y
^{231}Th	Thorium	β^-	25.64 h
^{231}Pa	Protactinium	α	3.25×10^4 y
^{227}Ac	Actinium	β^-, α	21.6 y
^{223}Fr	Francium	β^-, α	22 min
^{227}Th	Thallium	α	18.7 day
^{219}At	Astat	α, β^-	0.9 min
^{223}Ra	Radium	α	11.68 day
^{215}Bi	Bismuth	β^-	8 min
^{219}Rn	Radon	α	3.92 s
^{215}Po	Polonium	α, β^-	1.83×10^{-3} s
^{211}Pb	Lead	β^-	36.1 min
^{215}At	Astat	α	$\approx 10^{-4}$ s
^{211}Bi	Bismuth	α, β^-	2.16 min
^{207}Tl	Thallium	β^-	4.79 min
^{211}Po	Polonium	α	0.52 s
^{207}Pb	Lead	Stable	—

well as experiments on animals, we learned about health effects of uranium on humans, and ionizing radiation exposure in general, more than we know about the impact of any other dangerous substances or agents.

The chapter characterizes in some detail the relevant important *milestones in the history of uranium*, including its importance and beneficial use in many areas as well as its potential health effects due to the internal and external exposure coming from uranium alone and also from its numerous decay products where, for miners and the population at large, radioactive radon gas plays a crucial role. The results and consequences of a number of epidemiological studies, especially those carried out in the former Czechoslovakia and recently in the Czech Republic, are also summarized and discussed.

2 History of Uranium and the Role of Jáchymov

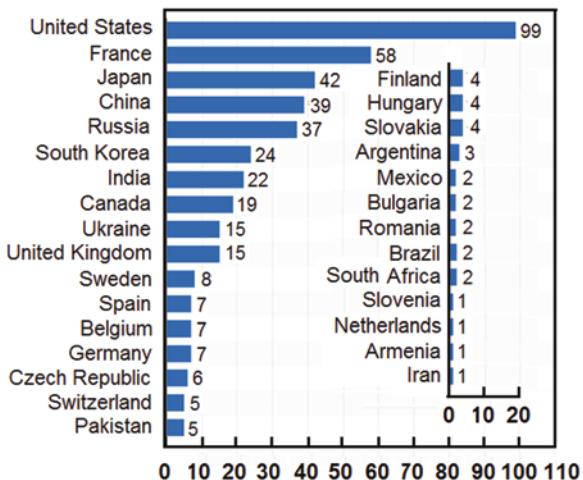
2.1 Some Important Uranium Milestones

The following milestones (DOE 1994; CC 2018; WNA 2018a) indicate the significant role uranium has played historically:

- 1789: Martin Klaproth (1743–1817) discovered uranium in uraninite ore from the Ore Mountains and named it after the planet Uranus discovered shortly before. In fact, the discovery was related to uranium oxide rather than a pure element, which was isolated only later in 1841 by Eugen Péligot (1811–1890).
- 1896: Henri Becquerel (1852–1908) observed that the pitchblende (from the Jáchymov area) caused a photographic plate to darken. This experiment resulted in the discovery of alpha and beta particles; gamma radiation was discovered later in 1900 by Paul Villard (1860–1934).
- 1898: Marie Curie-Sklodowska (1867–1934) and her husband Pierre Curie (1859–1906) first introduced the words “radiation” and “radioactivity”. Their discoveries included polonium and radium.
- 1900: Friedrich Dorn (1848–1916), a German chemist, during his experiments with radium decay chain discovered radon.
- 1902: Ernest Rutherford (1871–1937) concluded that radioactive decay is related to a spontaneous event followed by the emission charged particles by the parent nucleus, creating a daughter element which may also undergo a similar decay.
- 1905: Albert Einstein (1879–1955) put forward a theory relating mass and energy by a famous equation $E = mc^2$.
- 1911: It was confirmed the existence of various isotopes (with the same chemistry) of the same element.
- 1913: The first use of radium for the treatment of patients.
- 1920s: Radioactive dyes from Jáchymov became profitable export items used for luminous wristwatches.
- 1932: James Chadwick (1891–1974) discovered the neutron.

- 1934: Enrico Fermi (1901–1954) demonstrated the ability of neutrons to split atomic nuclei.
- 1938: Otto Hahn (1879–1968) and Fritz Strassman (1902–1980) discovered nuclear fission which verified the validity of the famous Einstein's equation $E = mc^2$.
- 1939: Frédéric Joliot-Curie (1900–1958) with his team demonstrated that the fission of uranium
- 1941: Glenn Seaborg (1912–1999) and his research team discovered plutonium.
- 1942: Enrico Fermi and Leo Szilard (1898–1964) demonstrated the first self-sustaining nuclear fission reaction (at the University of Chicago).
- 1942–1945: Under the Manhattan Project, the first nuclear bomb was built. In 1945, two bombs were used for bombarding Hiroshima and Nagasaki in Japan. The first of them used highly enriched ^{235}U , while the second one was based on ^{239}Pu extracted from uranium irradiated in a nuclear reactor.
- 1949: The Soviet Union tested the first two atomic bombs at a test site near Semipalatinsk (now in Kazakhstan).
- 1952: The inhalation of radioactive aerosols was found as the cause of “Jáchymov miner’s disease”.
- 1952: The UK tested its first atomic bomb.
- 1954: In Obninsk (near Moscow), the USSR began operation of the world’s first grid-connected nuclear power plant (5 MW).
- 1955: The first United Nations International Conference on the Peaceful Uses of Atomic Energy took place in Geneva, Switzerland.
- 1957: The UN officially formed the International Atomic Agency (IAEA).
- 1960: France tested its first atomic bomb.
- 1964: China tested its first atomic bomb.
- 1968: The Nuclear Non-Proliferation Treaty (NPT) was signed.
- 1970: Altogether 84 nuclear power reactors were operated in the world. Their combined electricity generation capacity was about 17,700 MW.
- 1974: India tested its first nuclear bomb.
- 1979: An accident happened at the Three Mile Island nuclear power plant (Harrisburg, Pennsylvania, USA) resulting in a limited core meltdown.
- 1980: In the world 245 nuclear power reactors were producing electricity with the combined generation capacity amounted to 133,000 MW.
- 1986: An accident at the Chernobyl nuclear plant with serious consequences of spreading radioactive material into the environment occurred.
- 1990: In the USA, 110 nuclear power plants generated electricity surpassing all fuel sources combined in 1956.
- 1990: There were altogether 416 nuclear power reactors in operation in the world; their combined electricity generation capacity was about 318,000 MW.
- 1998: Pakistan detonated its first nuclear weapon.
- 2000: Worldwide, 435 nuclear power reactors were in operation with a combined electricity generation capacity of 349,999 MW.
- 2010: On the whole, 441 nuclear power reactors were operated in the world; their combined electricity generation capacity was about 375,300 MW.

Fig. 2 Number of operable nuclear reactors as of June 2018, by country (based on (STATISTA 2018))



- 2011: An accident, comparable to the Chernobyl nuclear disaster, occurred at the Fukushima Daiichi nuclear power plant in Japan initiated by the tsunami wave reaching more than 10 m following the massive earthquake in the Pacific at the distance about 130 km from Fukushima. The tsunami put out of the operation backup electrical generators used for supplying power for the reactor's cooling system.
- 2018: In February, the total number of nuclear reactors in all countries which are operating nuclear power plants reached 448 (Fig. 2). At present, there are altogether 58 nuclear reactors under the construction (most of them are in China with 18 reactors).

2.2 Early Mining Period

Jáchymov, before 1918 *Sankt Joachimsthal* or *Joachimsthal* (Saint Joachim's Valley), is situated on the Czech slope of the Ore Mountains (Krušné hory in Czech, meaning cruel mountains). The town, near the present-day German-Czech border, was founded in 1516. Its location is shown on the map in Fig. 3. This was in the time when an ore rich in silver was found in its surroundings. The silver mines were extremely lucrative with ore concentrations being very high.

This brought enormous prosperity to the town which in 1534, with a population of close to 20,000, became the second largest city in the Kingdom of Bohemia after Prague (then slightly above 50,000 inhabitants). At that time, more than 9000 miners lived and worked in over 900 mines in the Jáchymov area. The Jáchymov ore deposit was one of the largest deposits of silver within Europe in the sixteenth century.

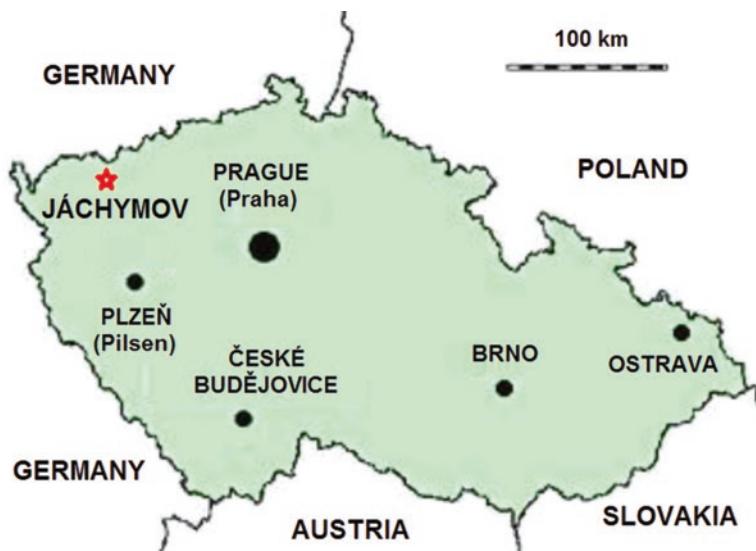


Fig. 3 The location of Jáchymov in the Ore Mountains (Erzgebirge) on the border between what is now the Czech Republic and Germany

Mining settlement known since 1517 as Jáchymov won in 1520 the status of a *free royal mining town*. After several years, the district became soon one of the most important producers of silver on the continent.

In 1520 a mint was set up in Jáchymov; the coins that were minted here were called by the German name “thaler”, later “tolar” (Fig. 4). Not many people are aware that the *dollar*, probably the most popular currency in the world, derived its name from an ancient silver coin from Jáchymov.

At the time of Jáchymov’s flourishing, the town attracted a number of then very important personalities, among whom was doctor Georg Bauer (1494–1555), better known by his Latin name *Georgius Agricola* (Fig. 5a). He was a reputable renaissance scholar from neighbouring Saxony. After studying at the University of Leipzig, he continued to study medicine in Bologna, Venice and Padua. Agricola was initially drawn to the mines of Jáchymov, intending to discover medical drugs from the ore. Later he abandoned the idea and fully devoted his time to visiting the town’s mines and smelters.

The mining in the Ore Mountains, separating Bohemia and Saxony, had been going on since the 1200s. Later, as of 1470 silver mining began very profitable and contributed to the wealth and prominence of the area. At the beginning of 1500,



Fig. 4 The Joachimsthaler, minted in Jáchymov, at that time the Kingdom of Bohemia, had (a) a picture of St. Joachim on one side and (b) the Czech lion together with the name of King Ludovicus on the other side (Wikipedia 2018)

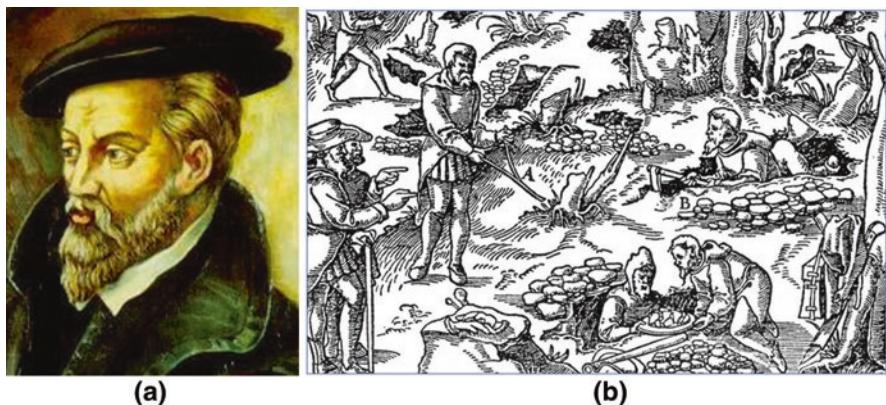


Fig. 5 Georgius Agricola (a) and one of many drawings from his famous book on mining showing prospecting work (b)

some reports about increased frequency of unknown disease among miners appeared in Agricola's writings. It took more than 350 years before this disease was diagnosed as lung cancer. At that time, however, it was not clear what caused this disease. It was only in 1925 when the so-called Schneeberg lung cancer was recognized as one of occupational diseases.

Agricola spent 4 years (1527–1531) in Jáchymov, where he worked as an urban doctor and pharmacist. Even after returning to Saxony, he quite often visited the town to collect and refine his knowledge of mining, metallurgy and mineralogy. Agricola's famous book, reflecting his lifetime work, was *De Re Metallica libri XII—Twelve books on mining*. The work presented 289 detailed woodcut illustrations; one of them depicting prospecting work is shown in Fig. 5b. For the

next 200 or more years, this work was considered as the miner's bible on metallurgy and mining. For centuries it was widely used as a sort of manual for mining ores and their metallurgical processing. He is considered *the father of mineralogy* (René 2018).

In the early seventeenth century, the silver ores were exhausted, and attention turned to nickel, cobalt, bismuth and arsenic. The mining interest gradually shifted later to uranium and radium. In the years that followed, some more compounds extracted from uranium ore were found to serve as a substance which could be used for painting on glassware or porcelain and some other materials, producing colourful, shining images. Ironically, it was from the "worthless" residues of the uranium extraction process that *M. Curie-Sklodowska* separated, at that time, a miraculous new element, she called radium. I radium is mixed with zinc sulphate; this compound could glow in the dark.

Moreover, uranium, when added to glass in conjunction, produces amazing yellow and green colours and fluorescence effects. Uranium paints attracted attention of many producers of glassware and pottery. Especially popular were articles such as vases and various decorative figurines (Fig. 6). The content of uranium varied from very tiny concentrations, well below 2% to around 25% of uranium. In the latter case, the external gamma radiation emitted by uranium decay products was likely not negligible. This was why the use of uranium paints is now extremely rare. Old items coloured by uranium are today considered antiques or retro-era collectibles.

This application of various uranium oxides helped Jáchymov to overcome the crisis after silver mining proved to be unprofitable. The business became so successful that several factories were built to satisfy the increasing demand for such commodities. Gradually, some other uranium colours for the *glassmaking industry* (orange yellow) and the "black uranium colour" for the porcelain industry were developed (Wikipedia 2018). Photos of two such factories in operation at the turn of the eighteenth and nineteenth centuries are shown in Fig. 7.

While in 1853 about 85 kg of uranium colours were produced in Jáchymov, in 1886 it was already 12,776 kg. At this time, the local factories were famous, and the



Fig. 6 Some examples illustrating the use of uranium, usually in oxide diuranate form, added to a glass mix before melting for colouration

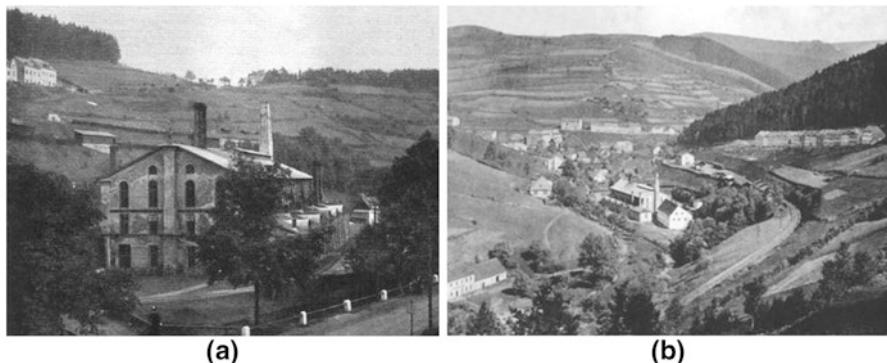


Fig. 7 A view of two uranium factories in Jáchymov (a) built towards the end of the nineteenth century and (b) erected at the beginning of the twentieth century



Fig. 8 Jáchymov, (a) a view of the town (around 1895) with a prominent building being the church of St. Joachim and (b) the former mint restored to serve now as a museum

world press referred to them as a total sensation. They were the largest factories of their kind in the world specializing in such products. By 1898, a total of 108 tonnes of uranium paints had been produced, of which the clear majority went for export.

The areas of the *Ore Mountains*, which historically always formed a border between Saxony in Germany and Bohemia (the Czech Republic), were known to be rich in various ores. It started especially with silver and then with uranium mining. Central European uranium deposits were the first industrially mined deposits in the world. A panorama of Jáchymov as it looked towards the end of the nineteenth century is shown in Fig. 8a. It illustrates the most famous sights of the town and reflects its former glory. The Royal Mint (Fig. 8b), a renaissance structure, has been preserved in its entirety. The building serves now as a museum displaying the history of the town, geology, mineralogy, minting and the spa industry.

2.3 Radioactive Era

Although the use of uranium compounds in glass and porcelain products continued well into the first decades of the twentieth century, Jáchymov's future was dramatically changed by the discovery of radioactivity by *Henri Becquerel* in 1896 and especially by the discovery of radium and polonium in 1898 by *M.e Curie-Sklodowska* and her husband, *P. Curie*. In fact, H. Becquerel was at one time the teacher of Marie Skłodowska when she came from her native Poland to Paris to study physics and mathematics. These three scientists made their discoveries when experimenting with unprocessed uranium ore (pitchblende) brought from Jáchymov.

Radium was considered to be a miracle substance able to cure cancer and to be used in many other medical applications, where it was believed to have magical curative effects. Since the extraction of radium from uranium ore was extremely complicated and hard work, its price skyrocketed up to US\$ 120,000 for a single gramme (approximately US\$ 2.2 million in today's values) in the first two decades of the twentieth century. In the late 1930s, however, the price fell dramatically.

Figure 9 shows some uses of radium as ingredients added to various substances and even to water and foodstuffs. It was promoted as a cure for most diseases or conditions.

Fortunately, the concentration of radium or its amounts in these materials or water was relatively low, which in most cases resulted in exposures to persons below the threshold level for deterministic biological effects (tissue reactions). This was why, for some time, no deleterious consequences had been noticed. The doses received by users were rather low, but sufficiently high compared with the current radiation protection requirements and the limits set by regulatory authorities for the public in accordance with international standards. In general, such applications of radioactive sources would now be found unjustified and thus forbidden.

The Jáchymov radioactive spa was founded in 1906, when very small-scale private baths were put into operation. At that time there were only small baths. Miners had to bring radioactive water in wooden buckets. Radioactive water baths have been in use since 1906 in Jáchymov and, only later, from 1912 in Bad Brambach



Fig. 9 Examples of various applications of radium promising miraculous effects or cures

and from 1918 in Oberschlema, Saxony. The business increased from 30 patients in 1906 to 228 in 1908. Although the increase in numbers indicates that the treatments were considered successful, real improvements would be rather difficult to assess considering the present standards and knowledge.

In 1912 the construction of the splendid *Radium Palace*, specializing in various treatments including radon and using radon baths, was completed. The Palace was situated near the well-known uranium factory that produced the uranium yellow, widely used at that time for colouring glass and ceramics (Fig. 10) (Marshall and Marshall 2008). The Radium Palace Spa Hotel, its other name, was the very best Europe could offer for this specific treatment at that time. Therefore, it attracted many celebrities from political, industrial and cultural life. The radon spa became renowned throughout the world.

The present view of the Radium Palace is shown in Fig. 11. Even after closing the Jáchymov uranium mines in 1964, the spa tradition has continued to today. Several other modern spa facilities meeting the highest standards have been built.

The magnificent Radium Palace Spa Hotel, known also as the Radium Kurhaus or Radium Kurhotel, offered 350 rooms, 85 bathrooms and the latest in modern conveniences and radium treatments, including its own baths, drinking cures and an emanatorium (inhalation) room. With the quality of the accommodation and the thoroughness of the treatment, Jáchymov continued to grow as a spa town, increasing the number of patients it saw in a year by huge numbers. Soon other hotels were being built in the town and surrounding areas.

These two spa hotels bear the names of two distinguished persons who were closely associated with Jáchymov, namely, famous Marie Curie-Sklodowska and

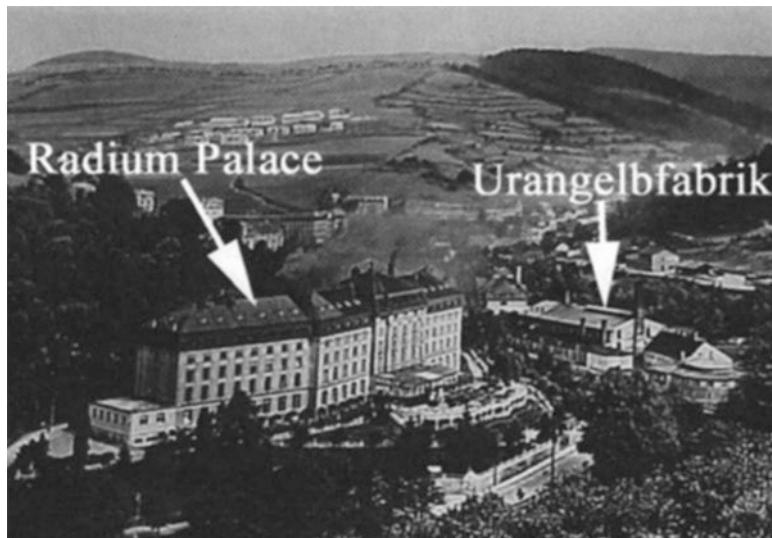


Fig. 10 This photo taken in 1915 shows the Radium Palace and the nearby factory (Urangelbfabrik) famous for producing uranium yellow



Fig. 11 The Radium Palace today after some renovation and modernization

the well-known Czech scientist and educator, Professor *František Běhounek* (1898–1973). F. Běhounek, who spent 2 years at M. Curie's Institut du Radium in Paris (1920–1922), and after returning home, studied radioactivity in the Jáchymov mines and became a pioneer in the use of radium. He was the director of the National Radiological Institute in Prague (1929–1946). In 1963 he founded the Department of Dosimetry and Applications of Ionizing Radiation at the Faculty of Nuclear Sciences of the Czech Technical University in Prague (by the way, the author of this chapter was one of the first graduates from this department, which he also later headed for some time). He also was the founder and the first director of the Institute of Dosimetry of the Czech Academy of Sciences in Prague.

F. Běhounek continued his close contacts with his Paris mentor. He accompanied M. Curie during her visit to Prague and Jáchymov in 1925 (Poledníček 2015). During her visit, Marie Curie was also received by the president of the republic, T. G. Masaryk. In Jáchymov she visited the Radium Palace and even went down into the pit of the Svornost (Concord) Mine.

In addition to the already mentioned use of uranium compounds in producing colourful glassware and ceramics, radium mixed with the zinc sulphide was another application of a newly discovered radioactive element (Braunbeck 1996; EPA 2016). Some of these items were made and sold without any restrictions since at that time the health effects of radiation were not fully recognized. At the beginning of the nineteenth century, people were fascinated by its mysterious glow. This paint containing radium was used in clock and watch faces and hands. Later, this glow-in-the-dark paint was also applied to airplane dials and gauges (Fig. 12).

In the years 1909–1937, the Jáchymov factory was able to produce as much as 64.3 g of radium. It was thought that radium possessed special curative properties. As mentioned above, the items where radium was used as an ingredient to produce special luminescent effects were not so dangerous for users since external radiation



Fig. 12 Uranium based colours, (a) an illustration of their uses on various types of watches and clocks and (b) an advertisement attracting attention to the “time at night”

emitted from such items was relatively low. However, later it was found that in some other similar factories, the workers engaged in the use of radium paints were in grave danger. Unfortunately, this was discovered only after some time when the consequences of internal exposure became visible and had produced terrible health effects. Radium, as an alpha emitter, is characterized by extremely high radiotoxicity since all energy of the radiation is absorbed in small volumes of tissues inside the body. This was the case of the so-called radium girls in the USA (Laurence 1979; Clark 1997; Abrams 2011).

The fine yellow powder which contained only a minuscule amount of radium was mixed with zinc sulphide, with which the radium reacted to give *a brilliant glow*. The effect was breathtaking. The demand at such factories showed no signs of slowing; more and more girls were recruited to paint dials. They used luminous radium paints to make the numbers on watches, clocks and aeronautical *dials glow brightly in the dark*.

It is estimated that more than 4000 workers worked in various factories in the USA and Canada to paint watch faces with paints containing radium. The brushes would lose shape after a few strokes, so some supervisors encouraged their workers to point the brushes with their lips (“lip, dip, paint”) or use their tongues to keep them sharp. Because the girls were not aware of any danger, they painted their nails, teeth and faces for fun with the deadly paint. After some time, many girls who painted dials began to fall ill with a mysterious disease. It was later concluded that the main reasons behind this illness was extensive internal contamination of the *radium girls* as a result of applying the recommended technique they adopted (Fig. 13). During these operations, they often swallowed some paint containing radium. A number of these workers suffered from bone cancer, which usually affected their jaws. It was only in the 1970s, when radium was no longer allowed to use on watch and clock dials.

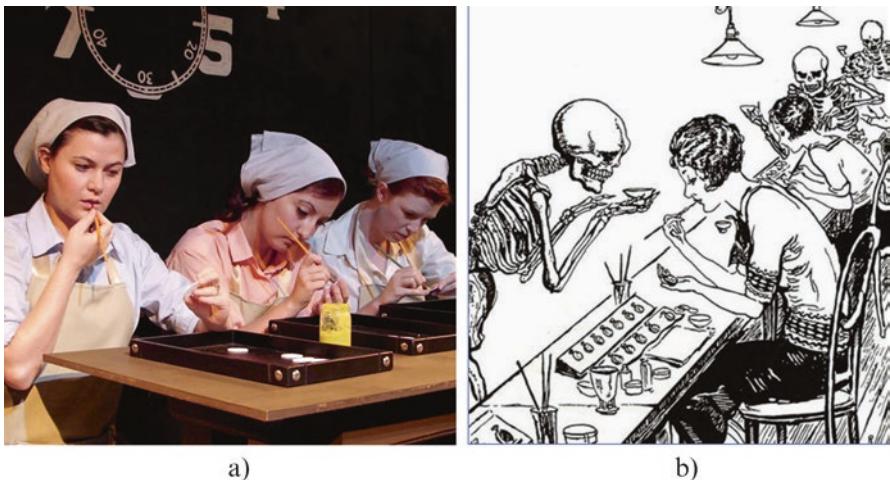


Fig. 13 Radium girls' dangerous job, (a) technique used in painting dials and (b) unfortunate consequences as illustrated in the contemporary press

2.4 Nuclear Age

While the start of World War I began to shake the golden age of radium in Jáchymov, the beginning of World War II brought some new attraction to interest in the uranium business.

Towards the end of 1938, the Otto Hahn (1879–1968) together with Fritz Strassmann (1902–1980) succeeded in *splitting uranium* atoms in two. For the first time, it was confirmed that nuclear fission was taking place. This discovery laid the basis for nuclear energy use but also for nuclear weapons. The small picturesque town of Jáchymov in a deep forest valley came to be known as the “cradle of the nuclear (atomic) age”.

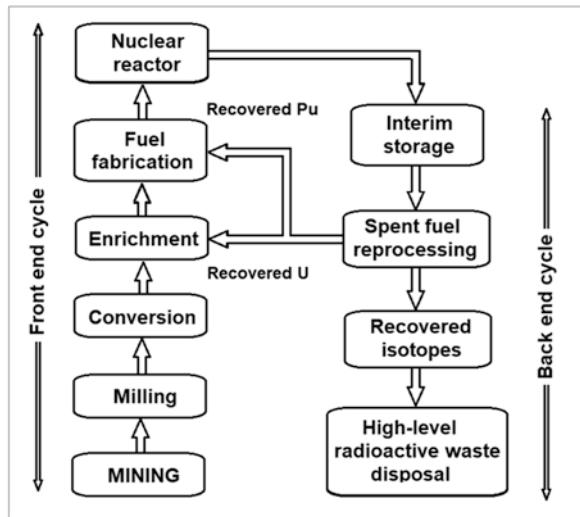
Since the beginning of World War II, further atomic research was characterized by the development of war-critical weapons. Some of the best scientists were hired to participate in the development of the atomic bomb in the years following 1939.

As of the end of World War II, uranium mining was intensified, both in Jáchymov and in other uranium mines in the former Czechoslovakia as well as on the German side of the Ore Mountains (at that time the German Democratic Republic).

Conventionally, uranium had been mined from *open pits* or *underground mines*. Later, alternate methods, such as in situ *leach mining*, based on injection of a specific solution into underground deposits to dissolve uranium, began to be common. The simplified scheme of the whole fuel cycle is shown in Fig. 14 (Hecht 2006).

It was found long time ago that uranium mining presents serious health hazard resulted in development of lung cancer due to inhaling uranium decay products (IEER 2018). Uranium mill tailings contain radioactive materials, notably radium and heavy metals, such as manganese and molybdenum, which can leach into

Fig. 14 Individual basic phases of the complete uranium nuclear fuel cycle



groundwater. Near tailings piles, water samples have shown levels of some contaminants at hundreds of times the government's acceptable level for drinking water. In situ leach mining leaves the unusable portion in the ground; it does not generate this form of waste. However, there is a danger of the contamination of underground water.

The town of Jáchymov soon after World War II became one of the Soviet Union's main suppliers of uranium for its nuclear weapons programme. In Germany, the USSR considered uranium mining a form of reparation. At that time, *Wismut* on the German side of the Ore Mountains employed at one time almost 500,000 people in various uranium mining activities.

Most of uranium ore used for the production of USSR nuclear weapons and fuel for nuclear power plants in the former Eastern Bloc was mined in East Germany (GDR) and former Czechoslovakia. The total production of uranium ore in GDR from 1946 to 2012 was 219,626 tU (tonnes of uranium). In Czechoslovakia, the total uranium production from 1945 to 2017 was 112,250 tU (René 2018).

The waste from the uranium enrichment process is called *depleted uranium* because most of ^{235}U was extracted from it. Depleted uranium found its use by the military, where at high impact speed, the density, hardness and pyrophoricity of the projectile enable the destruction of heavily armoured targets (Claussen et al. 2012).

2.5 World Production of Uranium

At present, uranium ore is mined in about 20 countries worldwide. Most uranium comes from Kazakhstan, Canada and Australia, the production of which accounts for more than 60% of world output (Fig. 15) (WNA 2018b). The largest known

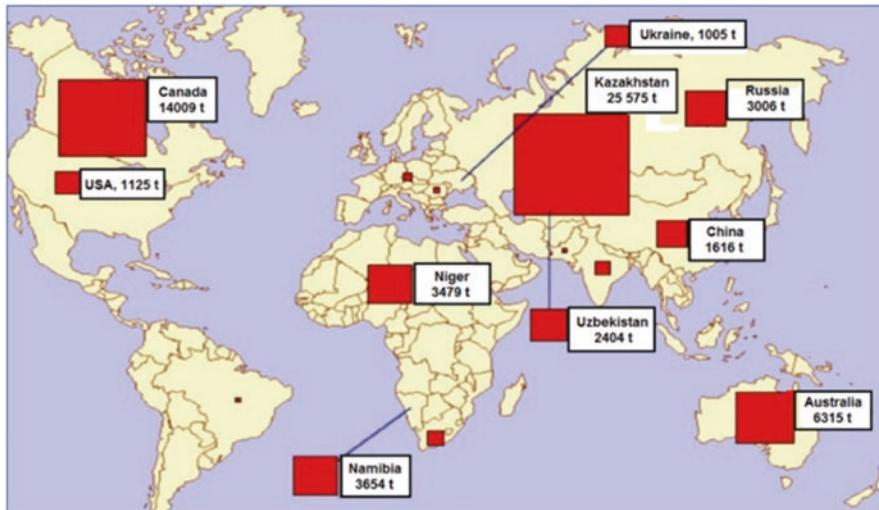


Fig. 15 Annual uranium production in 2016 in tU (U_3O_8) by major countries in the world

reserves of uranium are found in Kazakhstan; this Central Asian country produces more than 30% of the world's uranium, followed by Canada with an 18% share and Australia with 11%. The uranium production of Kazakhstan increased from 2000 to 2016 from 1870 to over 24,500 tU. Kazakhstan surpassed the previous leader, Canada, in 2009.

The uranium state industry in the *Czech Republic* was established on January 1, 1946, at the site of the old Jáchymov silver and uranium deposits. Following its start in 1946, exploration and mining grew rapidly and developed into a significant branch of industry. Although the total uranium reserves in the Czech Republic amounted to 135.3 ktU, the annual mining reached 252 tU in 2011. The Czech Republic was until recently the largest (and almost the only) uranium producer in the EU. There were altogether seven deposits of uranium on its territory; the last one where classic mining continued until 2017 was in the Rožná area (near Brno, the second largest city in the Czech Republic).

During the last decade or so, *prices of uranium* have shown the greatest instability in history—from a peak of US \$300 kg⁻¹ in 2007 dropping to US \$41 kg⁻¹ in 2016 (Fig. 16) (Gaspar and Mayhew 2018).

There are 15 countries, namely, Kazakhstan, Canada, the USA, Niger, Namibia, France, Uzbekistan, Ukraine, the Netherlands, Germany, Russia, Czech Republic, South Africa, Sweden and the UK, that exported the highest dollar value worth of natural uranium during 2017. These 15 countries shipped 99.997% of global natural uranium exports in 2017 by value (Workman 2018).

Obviously, as it is the case in any industry, in nuclear areas some failures or accidents may, in principle, occur. However, today all nuclear systems are so strictly secured and controlled that the probability that something like a new *Chernobyl*



Fig. 16 Historical price of uranium from 1997 to 2017 (based on www.indexmundi.com)

or *Fukushima* will most probably not happen. Even if an accident happens, there are new means and procedures, including sophisticated emergency preparedness and response, which will be able to mitigate any significant consequences of any nuclear mishaps. In addition to the unintentional failures due to material, instruments, software or even human failure, one must consider also cases when accidents are caused deliberately or high activity radioactive material is used for the construction of a radiological dispersive device (or a so-called dirty bomb). Under the present volatile situations in some regions in the world, the danger of radiological terrorism committed by individual radicals or organized terrorist groups cannot be underestimated.

While on one hand, uranium fission and radionuclides offer tremendous benefits to mankind, on the other hand nuclear energy could be abused against humanity. The most feared of possible scenarios of the future development is the one in which terrorist groups would be able to acquire weapons of mass destruction. During the decades of the *Cold War* people lived with a sense of possible nuclear apocalypse. The current international nuclear weapons control referred to as the “nuclear regime” to a large extent creates a framework in which nuclear weapons are currently under strict control, based mainly on the *Non-Proliferation Treaty* (NPT). Key to this effort is the UN Treaty on the Prohibition of Nuclear Weapons adopted on July 7, 2017. The treaty is considered as one of the landmarks in humanity’s short but troubling history with *nuclear arms*. This began in 1945 when the atomic bombs were used by the USA in bombing Hiroshima, on August 6, and Nagasaki, on August 9, 1945. The total number of casualties was estimated to be over 200,000 people.

The possible acquisition of nuclear weapons by the so-called rogue states presents a major challenge to the NPT regime. In this context, it is advisable to pay attention to the two most probable scenarios under which a conflict between the USA, or the US-led coalition, and some from troubled states and a confrontation of two actors with less nuclear potential. In a similar way, Russia may also be potentially involved in a similar nuclear conflict.

It appears that nuclear deterrence is among the most powerful tool against spreading nuclear weapons. There may be some countries interested in acquiring such weapons, but they are kept within some parameters, and they should be careful not to cross a certain line which would endanger the interests of the superpowers so that these powers would be ready to launch an armed conflict. So far, it is not probable that any terrorist organizations could obtain nuclear weapons since at present they would not be able to overcome technical difficulties and obstacles, including security measures aimed at safeguarding the nuclear arsenal. For terrorist attacks, terrorists will continue using rather different, cheap and sufficiently effective methods.

Although, in general it is felt that because of the efficient proliferation of nuclear material and other mechanisms adopted to minimize the use of nuclear weapons, there are some much less optimistic opinions. Even some high-ranking officials engaged in the field are rather sceptical about the efficiency of the present measures to prevent a nuclear conflict. For example, the executive director of the International Campaign to Abolish Nuclear Weapons (ICAN) has described the threat to humanity posed by nuclear weapons as “greater today than at the end of the Cold War” (Orphanides 2017). Some scientists and researchers are afraid that nuclear weapons systems could be vulnerable to cyberattack or that large-scale cyberattacks at particularly tense periods might result in escalation to a nuclear response. It may happen that a cyberattack could be carried out by a third party but attributed to the wrong state, leading to the initiation of a nuclear conflict.

There are currently nine states which possess nuclear weapons with an estimated total of around 15,000 missiles. Among those *nuclear weapon countries* belong the USA, Russia, the UK, France, China, India, Pakistan, Israel and North Korea. The biggest players in this group of countries are the USA and Russia, who hold by far the biggest stockpiles, estimated to be about 7000 warheads each (Fig. 17) (Ross 2016; Armstrong 2018).

3 Quantification of Uranium-Related Exposure

3.1 Basic Aspects

Uranium mining, milling and further processing involve some operations which contribute to potential adverse human health risks. This hazard is typically most pertinent to individuals occupationally exposed in mining industry; however, some

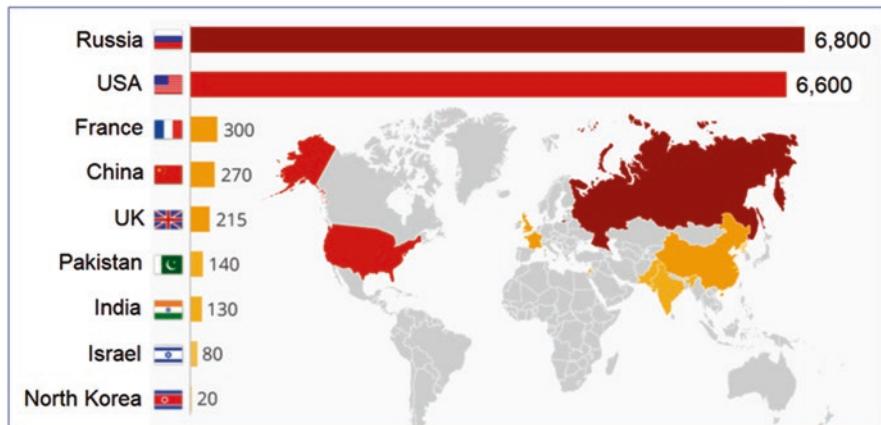


Fig. 17 The countries holding the world's nuclear arsenal (estimated warheads as of 2017)

exposures causing associated risks can also via environmental pathways result in the exposure of the public (NAP 2011; Keith et al. 2013).

In principle, persons may be mainly affected by the protracted exposure to *radon decay products* and by the exposure to external penetrating radiation.

Internal exposure to radioactive materials during uranium mining and processing occurs through inhalation and ingestion or through a cut in the skin. On the other hand, *external radiation exposure* (e.g., exposure to gamma photons and to the higher energy of beta radiation) can also contribute to a health risk.

It is obvious that only radionuclides present potential adverse human health effects. There are two other notable inhalation risks that are associated with silica dust and diesel exhaust. It has been recognized that cigarette smoking poses additional risk in absolute terms and there is potential for increased disease, including combined effects that are more than just additives. It is not easy to find out how these individual components affect the health of miners, and a question may arise about their synergic consequences.

Practically any applications of radiation or nuclear technologies result in most cases in some additional exposure of workers, members of the public and, in medical applications, also of patients. This exposure is considered undesirable, but one cannot escape it completely, although by and large such exposure is well below the dose limits or reference levels set by respective regulatory authorities (Sabol and Šesták 2017). This is the case in normal conditions when everything goes in accordance with the relevant safety regulations. Only in a rare situation the exposure may be higher, but this occurs only in the case of an incident or accident.

At lower radiation levels, only *stochastic biological effects* can be expected. These effects may occur after some time following the exposure in the form of cancer or genetic abnormalities. The probability of their appearance is directly proportional to the exposure in terms of the effective dose.

On the other hand, at exposures exceeding a certain threshold level, *deterministic effects* (tissue reactions) appear with the probability of 100%, while below these levels no such effects can be observed. Stochastic effects occur at exposures up to about several hundred mSv, while deterministic effects may begin at doses higher than about 0.5 Gy. For these two kinds of effects two different types of quantities should be used, namely, Sv and Gy, respectively.

The main aim of *radiation protection* is to reduce this exposure to the very minimum while allowing the utilization of the radiation for beneficial purposes. To control radiation exposure, one has to quantify it; therefore, quantities have been introduced to characterize the biological effects of the exposure that a person incurs.

The main quantity in radiation protection for assessing stochastic effects is the *effective dose* (E) defined as:

$$E = \sum_T w_T \cdot H_T = \sum_T w_T \sum_R w_R \cdot D_{T,R}$$

where H_T is the equivalent dose in the organ or tissue T and w_T is the tissue weighting factor relative to the organ or tissue T , w_R is the radiation weighting factor characterizing radiation of the type R and $D_{T,R}$ is the mean (average) absorbed dose in the organ or tissue T from radiation R . The unit of E is Sv (sievert), which represents a 5.5% chance of developing cancer. The average dose ($D_{T,R}$), as any other dose, is expressed in the unit of Gy (grey), which corresponds to the absorbed energy per unit of mass, i.e. J kg⁻¹.

The effective dose cannot be directly determined by monitoring; it can only be approximated by the *operational quantities* for *external exposure* and by assessment of the *intake of radionuclides via inhalation and ingestion* in the case of internal exposure. Therefore, we have to distinguish these two different types of exposure.

The external radiation contribution to the *total effective dose*, E_t , can be expressed by two measurable operational quantities, the ambient dose equivalent or the personal dose equivalent, while the ingestion and inhalation components have to be assessed based on the amount of radionuclides in terms of the activity taking into account relevant conversion factors, i.e.:

$$E_t = H_p(10) + \sum_j e(g)_{j,ing} I_{j,ing} + \sum_j e(g)_{j,inhalation} I_{j,inhalation}$$

where $H_p(10)$ is the personal dose equivalent at a depth of 10 mm in soft tissue during time period t , $e(g)_{j,ing}$ and $e(g)_{j,inhalation}$ are the dose conversion factors for the ingestion and inhalation of radionuclide j by age group g , respectively, and $I_{j,ing}$ and $I_{j,inhalation}$ are similar factors related to the intakes. In the abovementioned case, the information about the external radiation exposure is taken from personal monitoring. The results from workplace monitoring, where the ambient dose equivalent is assessed at a depth of 10 mm, namely, $H^N(10)$, can serve the same purpose.

Intake is generally defined as the process of taking radionuclides into the body by inhalation or ingestion or through the skin. The committed effective dose, $E(\tau)$,

is expressed using the contribution from ingestion and inhalation to the effective dose by integration over the time τ .

The present system of radiation protection is rather complicated, mainly because some new or modified quantities are quite often introduced, resulting in too many different quantities. This would probably be justified for research purposes, but for practical use it would be desirable to restrict the number of current quantities and rely mainly on those quantities which can be readily measured or monitored (Sabol and Šesták 2017).

In Fig. 18 (Sabol and Šesták 2017), the relation of all main quantities relevant for the assessment of stochastic and deterministic effects due to external exposure is illustrated. External radiation obviously is caused by particles or photons striking the surface of the human body from the outside, where the main quantity is the fluence defined as the number of particles or photons per unit of the area. The unit of this quantity is m^{-2} . The effective dose is obtained as a result of external radiation monitoring based on measurable operational quantities, namely, the ambient dose equivalent and the personal dose equivalent ($d = 10 \text{ mm}$). The equivalent dose in any organ or tissue can be assumed either by means of the average dose weighted by the appropriate radiation factor, or, in the case of the skin or extremities, it can be approximated directly by the personal dose equivalent at a depth of $d = 0.07 \text{ mm}$.

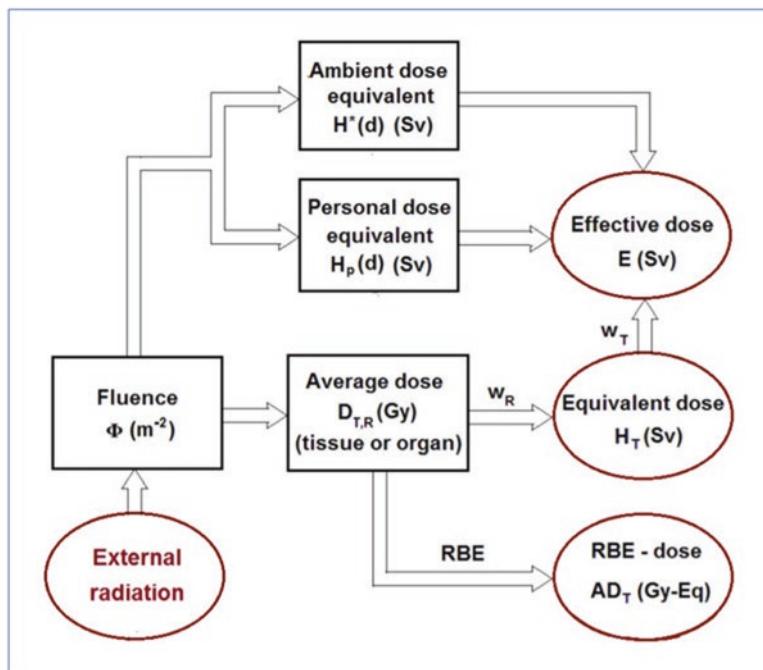


Fig. 18 Relations between various radiation protection quantities used to assess stochastic effects following external exposure (w_R and w_T are the relevant weighting factors)

There is a significant difference in quantifying the exposure due to *internal radioactive contamination*, i.e. caused by the emission of radiation from radioactive material which entered the human body through inhalation or ingestion, and exposure by radionuclides on the surface of the body, which may also be considered as a special case of radioactive contamination. The situation is schematically demonstrated in Fig. 19 (Sabol and Šesták 2017). Here the initial quantity is the *activity* (A) corresponding to the number of disintegrations which take place in a radionuclide per second. The basic unit here is s^{-1} , which has the special name Bq (Becquerel). The committed quantities based on the internal dose resulting from inhaling, ingesting or injecting radioactive materials are referred to as committed quantities. The integration time (commitment) in years following the intake τ is taken to be 50 years for adults and 70 years for children.

Considering the range of the radiation, it is obvious that external exposure is practically excluded for alpha particles and it is of marginal significance for low-energy beta particles. The main means of protection against external radiation is shielding, distance and time. It is worth noting that in the case of photons or neutrons (indirectly ionizing radiation), shielding cannot fully stop them but only reduce their number by attenuation.

As to the internal exposure, however, any radiation emitted by radioactive materials which enters the body can contribute to the absorbed dose inside the body. Once inside, radiation energy is deposited in cells, tissues and organs. The extent of

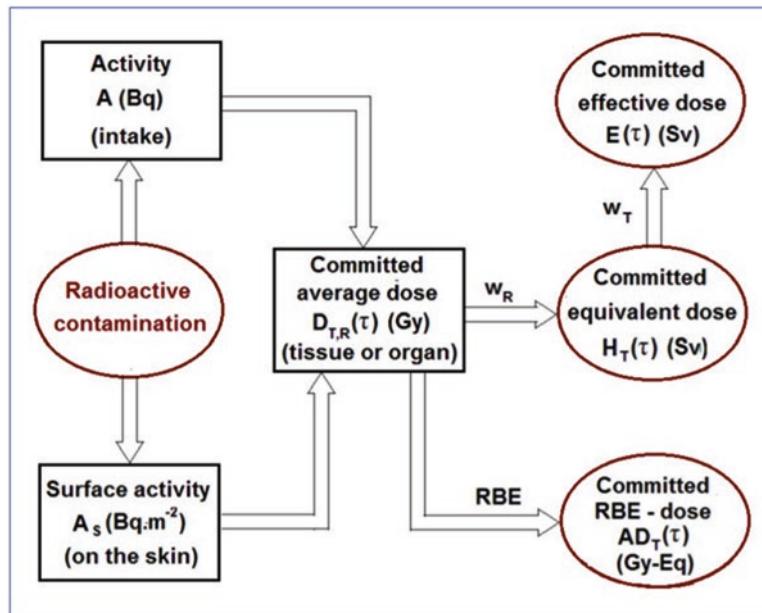


Fig. 19 Quantities characterizing personal exposure from the intake of radioactive material or from skin contamination

Table 2 ICRP detriment-adjusted nominal risk coefficient (10^{-2} Sv^{-1}) for stochastic effects after exposure to radiation at low doses

Exposed population	Cancer		Hereditary effects		Total	
	2007	1991	2007	1991	2007	1991
Whole	5.5	6.0	0.2	1.3	5.7	7.3
Adult	4.1	4.8	0.1	0.8	4.2	5.6

an internal dose is associated with the amount of radioactive material, which entered the body, where it goes in the body, how long it stays in the body and the type of radiation it emits.

The relevant risk coefficients have been proposed by the ICRP (Table 2) (ICRP 2007) for stochastic effects. The ICRP time to time upgrades these coefficients based on the latest scientific results. It can be seen that the combined detriment due to excess cancer and hereditary effects is about 5% per Sv. This is the same as $5 \times 10^{-5} \text{ mSv}^{-1}$, or 5 in 100,000 persons each exposed to 1 mSv or 1 in 20,000 (in the case of individual exposure 5 mSv).

In the uranium industry or any other uses of radiation or nuclear technologies, where under normal situations exposure is kept within the set limit and reference levels, there could be in principle rare cases (incidents, accidents, etc.) when this exposure may be elevated to reach threshold levels for deterministic effects. Figure 20 shows a simplified overview of what can be expected at such high levels of exposure, including the response of human organisms to indicated exposures.

3.2 Exposure of the Public

The population at large is generally exposed to both *natural radiation* and to *radiation from technological sources*, including uranium and its decay products. The effective dose to the population is on average more or less the same (the world average being of 2.4 mSv y^{-1}), although they may vary in different areas due to geological conditions (UNSCEAR 2017). On the other hand, however, the population radiation burden has been increasing substantially since about the year 2000. The main contribution comes mainly from medical diagnostic examinations, where the average annual number of these examinations is going up, especially in some developed countries. It is expected that this trend will also gradually affect the situation in many other countries in the world. The situation is illustrated in Fig. 21, which reflects the annual public average exposure in the USA, Germany and across the world. It is alarming that in 2006 the exposure of an individual in the USA was more than 6 mSv (Abbott 2015). One may expect that now (in 2018) this exposure is even higher.

More detailed information as to the contributions of individual components to the total exposure to the public in the USA is shown in Fig. 22 (NCRP 2009). It can be seen that the present contribution to the total public exposure due to natural and

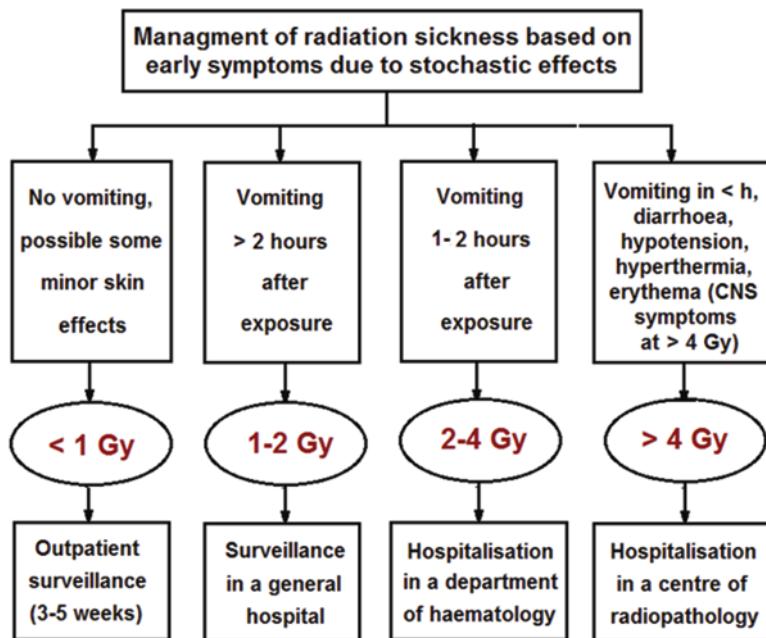


Fig. 20 Radiation sickness of persons having received high doses and their management (CNS central nervous system)

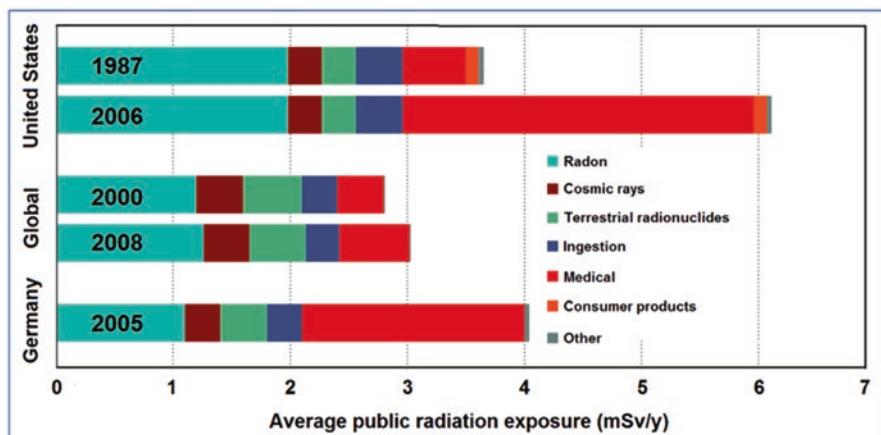
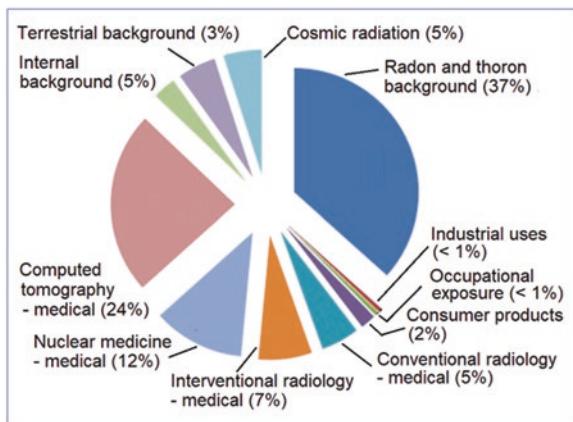


Fig. 21 The average annual exposure to members of the public in terms of the effective dose in the USA, Germany and worldwide in relevant years

Fig. 22 Percent contribution of various sources of radiation exposure to the total effective dose per individual in the USA for 2006



technological source is approximately the same. Not more than 30 years ago, the situation was quite different: natural radiation was responsible for about 85%, while the contribution from all other sources used in industry, medicine and other areas was about 15%.

Uranium, as a naturally occurring radionuclide distributed in the environment, also contributes to human exposure, although this exposure is under normal circumstances almost negligible. The control of the releases of radioactive material from mining and milling installations should be controlled and regulated by the operating companies in order to satisfy relevant national regulations for the protection of the public.

3.3 *Exposure of Miners*

Early uranium mining had not good safety record mainly because of lack of applying efficient protection measures against health hazards associated with the exposure to high level of radiation, toxic chemicals, crystalline silica and dust. At the beginning of extensive uranium mining in the 1950s, the occupational exposure often exceeded the present standards (20 mSv y^{-1}).

In addition to the hazards of conventional mining, uranium miners are at risk mainly because of the inhalation of radioactive dust containing radon, its decay products and other radionuclides present in uranium ore.

The nowadays uranium mining industry due to introduction of relevant safety measures is characterized by a good safety record. The results of radiation exposure of miners have shown that uranium workers do not receive doses higher than the dose limits introduced by relevant regulatory authorities (WNA 2018c). There are several approaches how to further reduce doses of *uranium workers*:

- To monitor and control dust in order to minimize the intake of gamma and especially alpha-emitting minerals. It is well known that dust presents the main cause of doses of workers in open-cut uranium mines and in mill facilities.
- To monitor and control strictly the personal doses of workers in the mine, plant and tailings areas.
- To ensure a sufficient natural ventilation to reduce the radon gas concentration.
- To introduce efficient hygiene standards imposed on workers and to use respiratory protection.

While the effective dose of miners can be substantially reduced by intensive ventilation and air filtration, there are rather limited means for the reduction of the gamma component to the total exposure. This can be demonstrated by the results of monitoring carried out at the Rožná uranium mine in the Czech Republic (Marušiaková et al. 2011; Sabol et al 2011a, b). This mine was in operation until 2017. The results during the last few years before it was closed showed that the most dominant component of the total effective dose was caused by the intake of long-lived radionuclides. They contributed to the total effective dose of miners to about 50%. The intake through inhalation of radon decay products and external gamma irradiation contributed to the total dose at about 30% and 20%, respectively. The individual average annual exposure among 600 miners was estimated to be around 8 mSv. In some other uranium mines, the exposure was found to be lower (UNSCEAR 2017).

In the assessment of the exposure of workers in uranium industry, it is necessary to differentiate between uranium miners from different mining activities and facilities. The highest dose is usually received by miners in underground mines (with average exposure from 5 to 10 mSv y^{-1}), while the workers engaged in uranium processing hardly exceed 5 mSv y^{-1} (Bouville and Kryuchkov 2014).

3.4 Pollution of the Environment and Its Mitigation

There is no doubt that uranium mining, processing and reclamation have certain potential impacts as to surface and underground water quality, soil, air and biota. There is no more uranium mining in Europe; emphasis is now concentrated on the rehabilitation of former production facilities. The currently undergoing *rehabilitation projects* in Germany (Wismut) and the Czech Republic (Stráž, Rožná and other sites) disclosed the range of problems that must be addressed.

It has become clear that the consequences of uranium mining and milling continue to be a problem requiring attention and appropriate remedial action. The situation was recognized especially at the end of the Cold War, after which more concrete steps were taken on a more massive scale.

The extensive uranium mining and milling in the past in the Czech Republic resulted in serious environmental problems including the contamination of groundwater. Following the 1990s an extensive environmental programme was set up. The

costs of all the remediation activities are presumed to be enormous (NRC 2011). The Czech government has committed to allocating nearly US\$ 2 billion for the remediation of legacy uranium mine sites through 2042.

It has to be emphasized that the uranium industry was developed at a time when no strict regulations concerning eventual end-of-life management were in place.

4 Results of Epidemiological Studies

The assessment of cancer risks associated with exposure to ionizing radiation was the aim of a number of *epidemiological studies*. Some of them concentrated on the health effects in uranium miners which resulted from their exposure to radioactive substances. A large proportion of the epidemiological studies were performed especially in the former Czechoslovakia, later in the Czech Republic, Germany, France, the USA and some other countries. These studies of uranium miners and millers included assessments of their exposure related to the uranium working environment. Most studies had difficulties in the reliable estimation of not only exposure but also other factors, including smoking and other toxic substances encountered in mines.

As early as in 1556, Agricola in *De Re Metallica* reported on a fatal respiratory disease in miners. It was only in 1879 that this disease was identified as lung cancer. Miners of uranium-bearing ores in the Ore Mountains of Central Europe were reported to have an unusually high frequency of *fatal lung disease*.

In assessing the impact of uranium-related risk, researchers use different terms and units depending on the aims of a particular study and their own preferences. It is desirable to distinguish between the quantification of external penetrating radiation and internal exposure delivered mainly through inhaled radon and its progeny. While external radiation can be evaluated using relevant operational quantities in mSv, for the assessment of internal exposure, other units were introduced, namely, WL and WLM.

The concepts used in assessing the risk caused by radon and its progeny are based on disease incidence. In this context, it is important to understand the *relative risk* (RR), *excess relative risk* (ERR) and *working level* (WL) as well as *working level month* (WLM) which is often used to quantify the exposure to inhaled radon and its decay products.

The relative risk represents a ratio of disease rates in exposed and unexposed groups of persons (dimensionless quantity). This can be interpreted using the following example: if the cancer rate in an exposed population is, say, 8 out of 1000, and in the unexposed population the rate is 4 out of 1000, the relative risk would be 8 divided by 4 or 2. The relative risk can be used to describe not only incidence but also mortality. On the other hand, the excess relative risk is introduced as the relative risk minus 1. In other words, the excess relative risk represents the increase in the risk of a disease compared to the background absolute risk in the absence of exposure.

In radon dosimetry another quantity called *working level* (WL) is still widely used. The unit WL was introduced in early days of radon (^{222}Ra) and radon progeny (primarily ^{218}Po and ^{214}Po) assessment and monitoring. Working level is a historical unit of concentration of uranium mining products of radon. One WL refers to the concentration of short-lived decay products of radon in equilibrium with 3700 Bq/m³ in air. By definition, 1 WL equals any combination of radon decay products which release potential alpha energy of 1.3×10^5 MeV in complete decay. In order to express the total exposure of a person, another unit is traditionally used, the *working level month* (WLM). This unit is equivalent to the exposure to radon progeny corresponding to the product of the progeny concentration in WL and the exposure time in nominal months. Inhalation of air with a concentration of 1 WL of radon daughters for 170 working hours results in an exposure of 1 WLM. An exposure of 1 WLM results in a dose from alpha particles to the lung of about 12 mGy to the critical target cells in the lung.

Several epidemiological studies to assess radon-related exposure have been organized. Many of these investigations took place in the former Czechoslovakia and later in the Czech Republic (Ševc et al. 1976; Horáček et al. 1977; Tomášek et al. 1994; Ševc et al. 1998; Tomášek et al. 2008; Tomášek 2012). One of those studies (Tomášek 2012) was based on 9978 Czech uranium miners with 1141 lung cancer deaths, and an updated follow-up 1952–2010 and corresponding to 31 years of mean follow-up was observed. These results were used to obtain more reliable estimation of the exposure–response relationship. The study was based on the investigation of a total of 9978 miners exposed in two different periods. The results are summarized in Fig. 23.

5 Conclusion

Uranium has played an important role in mankind's history. There have been a number of applications of this element and its numerous compounds and decay products in industry, medicine, science and many other areas. The most important use of the enriched uranium is in the production of energy by its fission. Unfortunately, uranium can also be used in weapons of mass destruction, which still present a potential threat to the planet.

Since radioactivity as well as the discovery of radium and polonium was made while experimenting with uranium ore from Jáchymov, this small town entered forever into the history of the modern nuclear age. Uranium from its deposits was also used for the Soviet Union's military industry which succeeded to follow the USA in producing nuclear bombs.

In earlier times, perhaps until the 1970s, uranium mining, milling and other aspects of the uranium fuel cycle were not considered a big environmental problem, and, in addition, the international standards and national legislations for ensuring adequate protection of workers and the public had not been so strict as they are nowadays. This is why it is necessary to deal with the uranium legacy and to

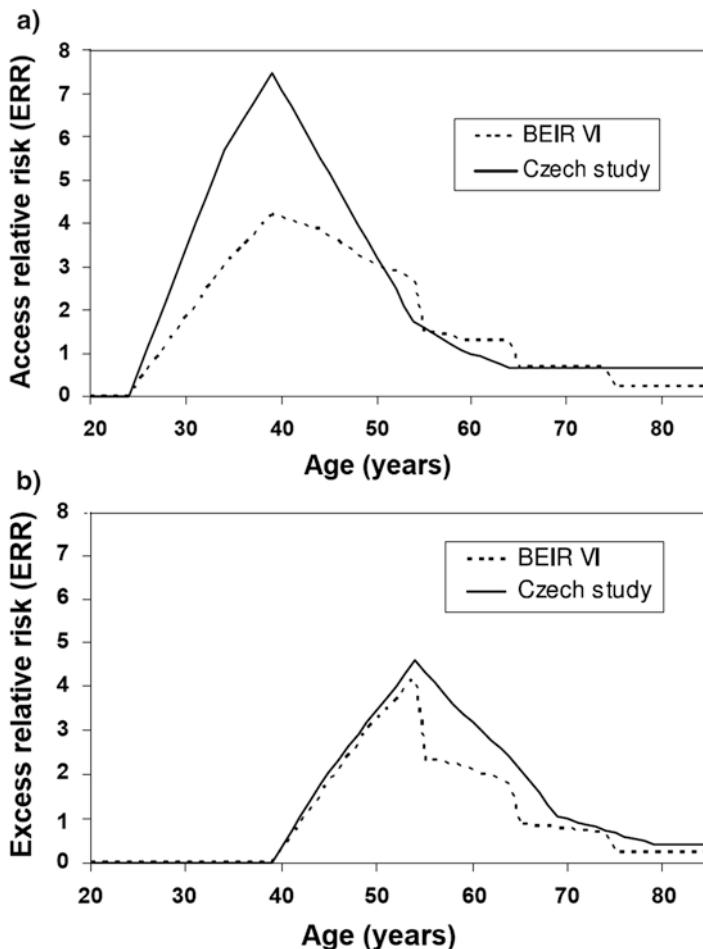


Fig. 23 Lung cancer ERR associated with cumulative exposure (8 WLM) received at ages 20–34 (a) and ages 35–49 (b) in dependence on age. Solid line, model derived from the Czech final model. Dashed line, model BEIR VI (Adopted from BEIR 1988)

make vast areas around uranium mining, milling and processing facilities which were found to be radioactively contaminated reach levels which exceed the present severe protection standards. Substantial funds have been allocated to return these areas to such conditions so that they can be returned to an environmentally acceptable level for normal exploitation. The decontamination process, which is aimed at keeping radioactive concentrations in soil, water and the air at permissible levels, is under implementation in many countries where uranium was mined, milled and processed.

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Uranium and Its Distribution in Typical Belarusian Soils



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Abstract The background levels of uranium content in the soil cover of different regions of Belarus are determined. Experimental data on the uranium content in the samples of (0–20)-cm layers of different varieties of sod-podzolic, sod, and peat-bog soils are presented. From analysis of the experimental data obtained, it follows that the uranium content increases in the series of soils “sandy-sandy loamy-loamy-clayey” as the content of fraction with the size of soil particles less than 10 μm increases. Natural background concentrations of uranium in the environment differ between various regions of the country. In accordance with the structure of the soil cover, there is an increased content of uranium in the northern region of Belarus with a higher proportion of loamy and clayey soils than in the southern region where sandy and sandy loam soils occupy a significant part of the territory. Experimental data on the uranium content in the soil interstitial (pore) water extracted from water-saturated soil samples by the method of high-speed centrifugation are presented. A close direct relationship was found between the portions of uranium and organic components in the soil interstitial solutions of their total content in mineral soil samples. The coefficients of uranium distribution between a solid phase and interstitial solution of soils of different types were estimated. For individual varieties of soils, it has been established how the uranium reserve in a mobile (conditionally biologically available) form changes with a change in the temperature and humidity of the soil.

Keywords Uranium in soils and interstitial (pore) solutions of soils · K_d coefficient · Mobile uranium species · Effect of temperature and humidity

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1 Introduction

Uranium belongs to terrigenous radionuclides and is relatively widespread in nature. In notable concentrations, it is found in many rocks and oceans. Uranium is mainly in a diffuse state, and its content in different parts of the Earth is not the same. According to the prevalence in the Earth's crust, uranium occupies the 38th place. The average content of uranium in the Earth's crust is 2.3×10^{-4} (wt. %) that higher than content of silver, bismuth, cadmium, and mercury. It is believed most of the uranium is concentrated in the Earth's crust and is not distributed evenly throughout the planet substance (Greenwood and Earnshaw 1997).

The content of uranium in the Earth's soils varies in the range of $0.7\text{--}10.7 \mu\text{g kg}^{-1}$ (Kabata-Pendias and Pendias 1989). In the upper horizons of the Russian Plain soils, the concentration of uranium is in the range of $0.7\text{--}1.8 \mu\text{g kg}^{-1}$ (Vinogradov 1950). The oceans contain about 10^{10} tons of uranium, and the average concentration of uranium in seawater is $3.3 \mu\text{g L}^{-1}$. In the surface waters, it is in the range of $0.01\text{--}5 \mu\text{g L}^{-1}$ and in groundwater $0.1\text{--}500 \mu\text{g L}^{-1}$ (Ivanovich and Harmon 1982).

Radionuclides of natural radioactive uranium series play an important role in the formation of a dose load of the population living in territories with a normal radiation background. Their contribution to the effective dose of internal human irradiation from alpha-emitting radionuclides of the Earth's crust is substantial (Vasilenko 2001; GN 2.6.1.8–27-2000 Radiation safety standards 2002; IAEA 2004). In this connection there is a need for information on the content of uranium in the components of the environment, from where it can enter the human body.

The most important elements of natural systems that have a significant effect on the redistribution of uranium in the biosphere are soil and natural waters. Therefore, data on the content of uranium in soil and soil waters are of interest.

The study of background levels of uranium content in the soil-plant complexes of Belarus is still at the initial stage. The main part of the available information on that problem is obtained in the 1950–1980s of the twentieth century and concerns the distribution of ^{238}U in soils, depending on the composition and landscape-geochemical conditions of the distribution of soil-forming rocks (Shagalova 1986; Gurskiy and Loseva 1989; Kuznetsov 1997; Lukashov 2002). In recent years, the results on behavior of natural uranium in forest biogeocenoses of the Minsk Upland were published (Anisova and Yakushev 2008).

Migration of any element from the soil to plants is mainly carried out in the forms in which they are present in interstitial (pore) solutions of soils in the area of root nutrition of plants. In soil pore solution, radionuclides are present in forms characterized by the highest capacity for geochemical and biological migration (Ovsiannikova et al. 2000). That is why information on the content of radionuclides in pore solutions of soils and on the stock of radionuclides in soils in the forms, in which they can enter into the soil waters, is of particular interest.

The increase in the technogenic load on ecosystems, which has increased significantly since the mid-twentieth century, including the widespread use of mineral fertilizers in agriculture, leads to changes in soil properties, content, physicochemical state, and mobility of radionuclides in soils. This can lead to a redistribution of

radionuclides in the environment and an increase in the content of radionuclides in those components that determine the intake of radionuclides in the human body.

One of the ways of radionuclide penetration into the human body is through trophic chains, in which the “soil plant” plays an important role. Information on the forms of radionuclides in the soil that determine the radionuclide intake to plants is undoubtedly of interest. The study of the behavior of natural and technogenic radionuclides entering into the ecosystems from anthropogenic sources makes it possible to control the radioactivity of the environment and to reveal the nature of the effect on the ecosystems of natural and introduced radioactivity.

Countries that develop nuclear energy, including Belarus, should have a reliable system of radiation monitoring. Current monitoring systems in economically developed countries allow monitoring radioecological situations. However, even the most advanced of them are not able to fully ensure the prediction of the radioecological state of the territories without assessing the parameters characterizing the mobility of radionuclides in ecosystems. When assessing and forecasting the radioecological situations, an assessment of the reliability of geochemical barriers that prevent the spread of radionuclides beyond the limits of their localization should be considered among the primary scientific and applied problems. In terrestrial ecosystems, the main barrier function is carried out by the soil cover, which has a determining effect on the intake of radionuclides into groundwater and surface water, vegetation and other ecosystem components, and ultimately to the human body. The properties of soil as a natural geochemical barrier that prevents the migration of radionuclides in terrestrial ecosystems are determined by its sorption characteristics and can be estimated from the distribution of radionuclides between the solid phase and the pore moisture of the soil. Such information helps to identify places with increased mobility of radionuclides and to assess the environmental consequences of the presence of radionuclides in the environment (Sokolik et al. 2012).

The redistribution of radionuclides in terrestrial ecosystems essentially depends on that part of the radionuclides that is reversibly bound in the soil with the components of the sorption complex. These are, as a rule, radionuclides located in the soil in ionic or molecular form and capable of passing from the solid phase to the pore waters of the soil and genetically related with them surface and ground waters. Radionuclides of soil pore solutions, most actively included in the processes of biogeochemical migration, can be identified as radionuclides in a migratory-active form. Radionuclides reversibly associated with the solid phase of the soil (exchangeable forms) compensate for the loss of radionuclides in the pore solution when interfacial equilibrium is disturbed (intake of radionuclides into groundwater and vegetation assimilation), seeking to restore the disturbed equilibrium. In terrestrial ecosystems, the migratory-active, exchangeable and mobile (biologically accessible) radionuclide species are among the main indicators determining the migration properties of radionuclides in the soil-vegetation cover.

The state and mobility of uranium in the soil-vegetation cover depends significantly on the characteristics of the soil. Long-term changes in meteorological conditions affect the properties of the soil (The Second Congress of the Soil Science Society 1996; Loginov et al. 2010). The most significant meteorological parameters

include the temperature of the environment and the amount of atmospheric precipitation. Changes in temperature and humidification conditions significantly affect the thermal conductivity, water capacity, water permeability, humus status, and microbiological activity of the soil, on which acidity, redox potential, and other soil characteristics depend (Hanson 1985; Ovcharenko 1996; Titayeva 2005; Vodyanitskiy 2011). It should be expected that changes in the properties of the soil environment will also affect the species of natural and technogenic uranium in the soil. Content of mobile uranium species in the area of root nutrition of plants can change, which inevitably will affect the intensity of uranium accumulation in economically useful parts of plants, and therefore, the ecological quality of plant products (Ovcharenko 1996; Mansurov and Meleshin 2000). Evaluation of such changes is an important scientific and practical task, as, alongside with other factors, the competitiveness of the produced plant products in the world market is also determined by its ecological quality.

Studies on the influence of temperature and humidity of Belarusian soils on the uranium species were practically not carried out, although the results of such studies are undoubtedly of scientific and practical interest. Most of the research was devoted to the study of the influence of weather conditions on crop yields (Mansurov and Meleshin 2000; Loginov 2013). In recent years, some foreign researchers have begun to study the effect of sudden changes in weather conditions on soil characteristics, the state and behavior of radionuclides in the soil environment (Kovacheva et al. 2014; Milićević et al. 2017). The authors of these articles studied the effect of temperature and soil moisture on the uranium reserve in the forms that determine the availability of these elements to plants. For individual varieties of soils, it has been established how the uranium reserve in a mobile (conditionally biologically available) form changes with a change in the temperature and humidity of the soil.

2 The Nature (Origin) of Uranium in the Territory of Belarus

In the territory of the Republic of Belarus, there is uranium of natural and technogenic origin. In most of the regions, uranium of natural origin prevails, with a significant portion of it being uranium, imported into Belarus from Scandinavia during the glacial periods. In addition, the content of natural uranium in the soil depends significantly on the conditions of soil formation and the type of soil-forming rock (Kuznetsov 1997).

The origin of technogenic uranium is partly due to global fallout as a result of testing thermonuclear devices those began in 1952. This led to the entry of a large amount of uranium and transuranic elements (TUE) into the stratosphere (Ionizing radiation: sources and biological effects 1982; Perkins and Tomas 1985; Bocharov 1995).

The radioactive particles that enter the stratosphere remain in it for 1–2 years. They are spread by airflows throughout the stratosphere. Gradually, radioactive particles are carried to the troposphere and fall out on the Earth's surface with atmospheric precipitation. Stratospheric deposition leads to contamination of almost the

entire hemisphere in which the explosion was conducted. In addition to nuclear explosions, global uranium deposition on the Earth's surface is associated with accidents of artificial satellites equipped with nuclear and nuclear-isotope sources of energy. For example, the crash of the Soviet Cosmos-954 satellite in 1978 led to the release of several kilograms of uranium into the atmosphere (Bocharov 1995).

The level of global deposition of radionuclides on the Earth's surface depends on the geographical latitude. On the territory of Belarus, located at significant distances from the nuclear test sites, global fallout as a result of nuclear weapons tests had no significant effect on the content and isotopic composition of uranium in soils.

A large-scale study of the soils of Belarus on the content of uranium was carried out in the 1970–1980s of the twentieth century. Data on the ^{238}U content in the soil cover obtained as a result of this study are presented in the work (Shagalova 1986; Gurskiy and Loseva 1989). According to these data, the content of natural uranium in Belarusian soils is within 1×10^{-5} – 3.5×10^{-4} wt. %. The author (Shagalova 1986) distinguishes five groups of soils according to the level of ^{238}U : high (more than 2.0×10^{-4}), elevated ($(1.5\text{--}2.0) \times 10^{-4}$), medium ($(1.0\text{--}1.5) \times 10^{-4}$), reduced ($(0.5\text{--}1.0) \times 10^{-4}$), and low (less than 0.5×10^{-4} wt. %) uranium content. Depending on the type of soil, the uranium content varies widely. The lowest level of uranium ($(1\text{--}8) \times 10^{-5}$ wt. %) was found in peat-bog soils of the upper and transitional types and the most of all ($(1.6\text{--}3.5) \times 10^{-4}$ wt. %) in alluvial sod-gley loamy soils.

At present, the main amount of technogenic uranium in Belarus is connected with the accident at the Chernobyl nuclear power plant (ChNPP). Prior to the accident, the IV block of the Chernobyl NPP worked 865 days. It consisted of 1654 fuel assemblies. Most of the assemblies were first-load cassettes with a burn-out of 11–15 MW day kg⁻¹ U. In the active zone, there was also fresh fuel. The mass of uranium in the cassette was 114.7 kg, and the total mass of the fuel loaded into the reactor was 190.2 tons with an average burning depth of 10.3 MW day kg⁻¹ U (IAEA 1988).

There were two main stages of the Chernobyl accident. In the first stage, which lasted only a few minutes, as a result of significant overheating, nuclear fuel in the reactor underwent fragmentation. There was an explosive release of radioactive products from the reactor to a height of up to 2000 m (IAEA 1988). Many authors believe that at this stage some of the radioactive products got to the upper atmosphere and even to the stratosphere, which led to contamination of almost the entire Northern Hemisphere (Hirose et al. 1994). A composition of the radioactive products of this trace completely corresponded to the composition of the fuel of the IV block at the time of the accident. At this stage, the fuel was dispersed without melting and oxidation (Borovoy et al. 1990).

In the second stage of the accident, graphite burned after heating up the active zone, and in less than a day, the temperature reached the level, at which the release of radionuclides began. At this stage of the accident, fractionation of radionuclides took place. At the beginning of the second stage, volatile products were ejected, and then radionuclides were released on the combustion products and together with the fuel matrix. The high temperature in the second stage of the accident contributed to the partial oxidation of uranium dioxide and removal from the active zone of Cs, I,

and Te, which condensed on inactive carriers (soot, etc.) (Borovoy et al. 1990). During combustion of graphite, fuel particles depleted of volatile radionuclides were removed from the reactor. At this stage radioactive contamination of the territory of Belarus was formed (Konoplyya et al. 2007).

In the opinion of Konoplyya et al. (2007), the removal of the UO₂-based nuclear fuel from the emergency reactor occurred at relatively low temperatures not due to evaporation but as a result of dispersion and oxidation, proceeding with the formation of finely dispersed particles, in which uranium was partially in five and hexavalent state. Technogenic uranium is basically originated from Chernobyl, concentrated mainly within the Polesie State Radiation-Ecological Reserve (PSRER). In the rest of the country territory, there is mainly natural uranium, but use of mineral fertilizers, dolomite flour, and other reclaiming additives in the agro-industrial complex leads to additional amounts of uranium entering the soil.

During the oxidation process, the structure of the fuel particle was destroyed with the release of fission products, which stabilized in the intercrystalline space of uranium dioxide. The dispersion of fuel particles and the proportion of uranium oxides in higher oxidation states were mainly determined by the duration of the oxidation process (Loshchilov et al. 1992; Kashparov et al. 1995, 2003).

The contamination of the territory with actinides (including uranium) was extremely uneven and not only within the same region but also in the same settlement. This could be caused by the redistribution of radioactive products in the atmosphere and the peculiarities of their arrival on the Earth's surface under unequal meteorological conditions. Among the radionuclides emitted from the destroyed reactor, the maximum mass is accounted for by long-lived uranium isotopes—²³⁵U, ²³⁶U, and ²³⁸U. The presence of ²³⁶U in radioactive products, which is formed in significant quantities by the operation of a nuclear reactor of the RBMK type, indicates the presence of Chernobyl uranium. If the content of ²³⁹Pu in the Chernobyl release at the time of the accident (26.04.1986) is taken as unity, then the content of uranium isotopes with respect to ²³⁹Pu was: ²³⁵U, $(1.9 \pm 0.4) \times 10^{-4}$; ²³⁶U, $(1.0 \pm 0.3) \times 10^{-3}$; and ²³⁸U, $(3.1 \pm 0.6) \times 10^{-3}$ (IAEA 1988).

Under the condition of 5% fuel release from the emergency reactor, 9.5 t of uranium fell into the environment (Konoplyya et al. 2007). In general, the total emission of actinides on the territory of Belarus was approximately 2.5 times greater than their global deposition. Approximately half of the actinides fell on the territory immediately adjacent to the Chernobyl nuclear power plant, the rest was dispersed practically throughout the territory of Belarus. At the territory of the PSRER, the density of uranium deposition is from 18 to 100 Bq/m². The deposition of Chernobyl uranium on the surface of the soil could significantly affect the content and isotopic composition of uranium in the near zone. The ratio of ²³⁵U/²³⁸U and the proportion of Chernobyl uranium in the total uranium content in the (0–5)-cm soil layer at different distances from the destroyed nuclear reactor, established by mass spectrometric analysis by Konoplyya et al. (2007), is given in Table 1.

In the surface layer of the soil of the 30-km zone of the Chernobyl NPP and adjacent areas, the ratio of ²³⁵U/²³⁸U by mass exceeds the ratio of natural isotopes of uranium. The ratio of ²³⁵U/²³⁸U by mass for natural uranium is 0.00725 and for

Table 1 The ratio of $^{235}\text{U}/^{238}\text{U}$ by mass and the share of Chernobyl uranium of the total uranium content in (0–5)-cm layer of soil at different distances from ChNPP (Adopted from Konoplya et al. 2007)

Sampling site	Distance from ChNPP, km	Ratio of $^{235}\text{U}/^{238}\text{U}$ by mass	The share of Chernobyl uranium, %
Pogonnoye	27	0.00813 ± 0.00017	37.5 ± 0.8
Kryuki	15	0.00855 ± 0.00013	55.3 ± 0.8
Masany	8	0.00910 ± 0.00011	79.1 ± 0.9
Radin	20	0.00790 ± 0.00017	27.7 ± 0.6
Krasnoseleye	15	0.00819 ± 0.00019	40.2 ± 0.9
Borisovschina	55	0.00734 ± 0.00015	3.84 ± 0.08

Chernobyl reaches 0.0091. At the same time, the share of Chernobyl uranium in the total content of the element in the soil cover reaches 80% (Kudrjashov et al. 2002). The maximum ratio of $^{235}\text{U}/^{238}\text{U}$ is found in the soil of the former settlements Masany and Kryuki, most closely located to the accident site. In these sites, the content of Chernobyl uranium in soil cover exceeds the content of natural uranium by a factor of 1.5–2. With the distance from the Chernobyl NPP (ChNPP), the $^{235}\text{U}/^{238}\text{U}$ ratio approaches to the ratio of natural uranium isotopes. At a distance of more than 50 km from the ChNPP, the share of uranium of Chernobyl origin is less than 4% of the total uranium content in the soil, and at a distance of 100 km, it becomes negligible compared to natural uranium isotopes (Konoplya et al. 2007).

In the 30-km zone of the ChNPP and adjacent areas, the ratios $^{134}\text{Cs}/^{137}\text{Cs}$ and $^{238}\text{Pu}/^{239,240}\text{Pu}$ by activity, which are the criterion for the fuel burn-up, were kept constant (Kudrjashov et al. 2000, 2001, 2002). This indicates that nuclear fuel of approximately the same composition has fallen onto the territory of Belarus with an average content of ^{235}U of about 0.96% by mass. The constant isotope ratio of $^{235}\text{U}/^{238}\text{U}$ in the fuel-containing masses in the “Shelter” object, corresponding to the average degree of burnup (Reponen and Jantunen 1993), confirms this conclusion. In the soil of all the sites listed in Table 1, the average ratio of $^{236}\text{U}/^{238}\text{U}$ by activity was 0.34 ± 0.04 (Konoplya et al. 2007).

Thus, at present, in the territory of Belarus, there is uranium of natural and technogenic origin. Uranium of Chernobyl origin is concentrated mainly within the PSRER, in the rest of the territory there is mainly natural uranium.

It should also be noted that the widespread use of mineral fertilizers, dolomite flour, and other reclaiming additives in agriculture leads to additional amounts of uranium entering the soil.

3 Objects and Methods

The objects of the study were soil samples sampled in 2008–2017 in different regions of Belarus. Soil samples included the different varieties of sod-podzolic, sod, and peat-bog types of soils. In the FAO-UNESCO system, the alluvial soddy

soil type corresponds to fluvisol, the sod-podzolic to podsoluvizol, and the peat-bog to histozol.

For investigation of vertical distribution of uranium in soils, the soil sections were made on undisturbed plots using special stainless steel sampling equipment. The soils were sampled layer by layer using increments of 5 cm to a depth of 30–40 cm. For investigation of uranium species, the soils were sampled to a depth of 10 or 20 cm from the soil surface by a metal drill using the “envelope method” (five subsamples of soil were taken in the corners and in the center of plots). Soil subsamples from each plot were combined.

In laboratory conditions the soil samples were purified from plant fragments, carefully homogenized and sieved (2 mm apertures) and dried at a temperature of not higher than 40 °C.

The content of uranium in the samples was determined by the method of the radiochemical analysis (MN 1497–2001; IAEA 1989). The samples of soil were treated in a drying chamber at a temperature of 100–105 °C to constant weight and ignited in a muffle at a temperature of 600–650 °C. After mineralization the samples were destroyed using concentrated solutions of HF and HNO₃ and transferred into HCl solution. Uranium separated and cleaned from other elements using ion-exchange column with the AV-17 or Amberlite IRN78 (SUPELCO product) resin. Uranium converted to nitrates and additionally cleaned from elements of the iron group by extraction method using tributyl orthophosphoric acid (TBP). For extraction of uranium from tributyl phosphate to aqueous phase, o-xylene has been used. After reduction of U (VI) to U (IV) by TiCl₃, uranium was deposited on 0.1 µm pore size membrane filters using a cerium fluoride coprecipitation technique with 50 µg of cerium carrier. Identification of alpha-emitted isotopes of uranium was carried out by Alpha Spectrometer SOLOIST U0450 with ULTRA-AS detector installed and ruggedized low-background detectors 576 A-600 RV. The efficiency of the detectors was ~30%. The ratio energy-to-channel was 5.9 and 7.8 keV channel⁻¹. The energy resolution of the detectors was 30–40 keV. The content of uranium in the soil samples was determined in not less than four parallel subsamples. Uncertainty of ²³⁸U detection in soil samples was 6–11% depending on radionuclide activity in the samples. The radiochemical yield of uranium determined using alpha-emitting ²³²U as a tracer.

The content of total organic matter in the soil samples was determined by ignition of the air-dry soil samples in a muffle furnace at a temperature of 1023 K. Other soil characteristics were determined by conventional methods (Vorobyova 2006).

Interstitial (pore) solutions were extracted from water-saturated soil samples using a high-speed SIGMA-4-10 centrifuge (Ovsiannikova et al. 2000). The separated interstitial solutions were passed through a membrane filter with a pore diameter of 0.45 µm. The soil solutions were concentrated by evaporation in presence of a tracer ²³²U and analyzed for uranium content.

The concentration of organic components and the ratio of humic acid (HA) and fulvic acid (FA) fractions in soil solutions were determined from the optical density of HA and FA solutions after separation of organic components into fractions (Orlov 1990).

The content of exchangeable and mobile (conventionally biologically available) uranium in soils was established by selective extraction using solutions of 1M ammonium acetate (NH_4Ac , pH 7) and 1M HCl or acetate-ammonium buffer solution (pH 4.8). Soil samples were treated with an extracting solution at a ratio of “soil/solution” of 1:10 for 24 h, followed by the determination of uranium in the extracts obtained by radiochemical analysis. The acetate-ammonium soil extract simulates a soil solution with a neutral medium reaction, and the 1M HCl or acetate-ammonium buffer extract simulates an acidic soil solution at the boundary with the root system of plants (Frid 1996; Fedorov 2002). The sorption capacity of the soil with respect to uranium was estimated from the value of the coefficient K_d , which is the ratio between the activity concentrations of the solid phase and the interstitial solution of the soil in the state of interphase equilibrium in the system or close to it (Ovsianikova et al. 2000).

4 Vertical Distribution of Uranium in Soils

The objects of investigation were the mineral and organic soils sampled in August 2008–2010. The location of the sites, their geomorphological position, and the type of soil cover are given in Table 2.

The sampling sites differed in geomorphological position in the relief, humidification conditions, and soil cover type. The plots SP_{S1} and SP_{S2} are located within the floodplain of the river Pripyat. Plot SP_{S1} is far from the main riverbed, and SP_{S2} is near old riverbed that has lost connection with the basic riverbed. Plot P1 is within the bogged meadow in depression of above the floodplain terrace. During the spring and autumn floods, the areas are flooded. In this case, the SP_{S2} site for a longer period is in excess of waterlogging conditions compared to the SP_{S1} site.

The soil cover of SP_{S1} and SP_{S2} sites is formed on ancient alluvial and fluvioglacial sandy alluvium in conditions of temporary excessive moistening and dynamic water regime. The soil-forming rocks are characterized by high water permeability. During the spring and autumn floods, the water penetrates to a considerable depth. In periods between floods, groundwater in the SP_{S2} site is at a shallow depth from the soil surface.

In P1 and P2 plots under conditions of constant excess moisture, the marsh process of soil formation develops, which proceeds under anaerobic conditions. Under such conditions, with a general decrease in the activity of oxidation-reduction processes, the reduction processes prevail over the oxidative processes, and it leads to a weakening of the processes of mineralization of the organic matter of the soils. As a result, partly decomposed organic residues accumulate on the soil surface in the form of peat of different thickness. Under conditions of excessive moisture in the soils, gleying of the mineral rock takes place. Its characteristic feature is the conversion of ferric iron (III) to ferrous iron (II). The iron (II) compounds give the soil a bluish tinge. They are better soluble and more mobile than iron (III) compounds.

Under conditions of temporary excessive moistening, the iron compounds in the soils can be either in the ferric or in the ferrous form. In dry periods of the year, the

Table 2 Location, geomorphologic position, and soil types of plots

Plot	Location	Geomorphologic position	Soil type (FAO-UNESCO classification)
SP _{S1}	Khoiniki district Gomel region 51°32'11.8" N; 29°56'19.5" E	Floodplain of the Pripyat' river (far from the main riverbed)	Alluvial sod-podzolic sandy, gleyed in the bottom, placed on the alluvial and fluvial-glacial sands (Fluvisol)
SP _{S2}	Khoiniki district Gomel region 51°35'29.9" N; 29°50'50.7" E	Floodplain of the Pripyat' river (cut-off)	Alluvial sod-podzolic sandy, gleyed in the bottom, placed on the alluvial and fluvial-glacial sands (Fluvisol)
P1	Khoiniki district Gomel region 51°36'09.0" N; 29°59'39.9" E	Depression of above the floodplain terrace	Peat-bog (Histosol)
S _{SL1}	Lelchitsi district Gomel region 51°41'47.7" N; 28°04'35.3" E	Floodplain of the Uborot' river	Alluvial sod-gley sandy loam (Fluvisol)
P2	Lelchitsi district Gomel region 51°42'51.3" N; 28°04'48.0" E	Floodplain of the Uborot' river	Alluvial peaty-gley (Histosol)
S _{SL2}	Lelchitsi district Gomel region 51°45'24.7" N; 28°18'29.1" E	Floodplain of the Uborot' river	Alluvial sod-gley sandy loam placed on the sandy loamy alluvium (Fluvisol)
S _{SL3}	Lelchitsi district Gomel region 51°44'25.6" N; 28°29'51.5" E	Ameliorative canal	Sod-gley sandy loam placed on the water-glacial friable sandy sandy loams (Fluvisol)

upper part of the soil dries up, its air regime improves, and oxidative processes develop that lead to the formation of ferric hydroxides. Under conditions of constant excess moisture (in wetlands and in the location of groundwater), iron (II) reacts with silica and alumina to form secondary aluminofersilicates having a gray, greenish, or bluish color. When they accumulate in the soil, a gleyed horizon is formed (Kulakovskiy et al. 1974).

Alluvial soils develop in the river floodplains on alluvial sediments under the influence of prolonged flooding during the spring and summer-autumn floods. In conditions of temporary excessive moistening, semihydromorphic (Fluvizol) alluvial sod-gley soils (S_{SL1}, S_{SL2}, and S_{SL3} plots) are formed, and in conditions of constant excessive moistening, hydromorphic alluvial peat-bog (Hystozol) soils (P2 plot) are formed.

A change of the soil density, content of total organic matter, and activity concentration of ²³⁸U in the soil profiles are shown in Table 3.

Using the data of Table 3, the inventories of ²³⁸U in the soil profiles (Table 4) and the percentage of its total inventory (of the profile) associated with each soil increment were established (Fig. 1).

Table 3 Density (ρ), content of total organic matter (TOM), and activity concentrations of ^{238}U in the soils

Plot	Layer depth, cm	ρ , g/cm ³	TOM, % of dry sample mass	A_{U} , Bq kg ⁻¹
SP _{S1}	0–5	1.61	2.9	8.1 ± 0.6
	5–10	1.74	1.3 ± 0.1	5.2 ± 0.4
	10–15	1.69	0.8 ± 0.1	3.7 ± 0.3
	15–20	1.66	0.9 ± 0.1	4.4 ± 0.4
	20–25	1.79	0.8 ± 0.1	4.5 ± 0.4
	25–30	1.79	0.21 ± 0.02	5.0 ± 0.4
SP _{S2}	0–5	1.23	5.0 ± 0.1	6.2 ± 0.6
	5–10	1.53	2.8 ± 0.1	7.4 ± 0.6
	10–15	1.67	0.80 ± 0.08	5.0 ± 0.4
	15–20	1.33	0.79 ± 0.08	3.7 ± 0.3
	20–25	1.64	1.2 ± 0.1	3.1 ± 0.3
	25–30	1.57	0.80 ± 0.05	5.6 ± 0.5
P1	0–5	0.12	82 ± 1.4	2.4 ± 0.3
	5–10	0.21	79 ± 1	2.9 ± 0.3
	10–15	0.29	79 ± 1	3.1 ± 0.3
	15–20	0.31	80 ± 1	4.5 ± 0.4
S _{SL1}	0–5	0.30	9.0 ± 0.7	10.9 ± 0.8
	5–10	0.23	10.7 ± 0.4	12.0 ± 0.8
	10–15	0.37	2.3 ± 0.2	10.9 ± 0.8
	15–20	0.50	2.8 ± 0.1	10.6 ± 0.8
	20–25	0.42	1.0 ± 0.1	7.1 ± 0.6
	25–30	0.45	0.36 ± 0.03	6.2 ± 0.6
	30–35	0.41	0.30 ± 0.02	5.3 ± 0.5
	35–40	0.29	0.11 ± 0.01	4.5 ± 0.5
P2	0–5	0.10	26.3 ± 1.2	11.7 ± 0.9
	5–10	0.22	23.1 ± 0.3	9.4 ± 0.8
	10–15	0.34	14.2 ± 0.6	7.7 ± 0.7
	15–20	0.21	8.3 ± 0.4	7.5 ± 0.7
	20–25	0.27	3.3 ± 0.1	6.3 ± 0.6
	25–30	0.37	2.2 ± 0.1	6.8 ± 0.6
	30–35	0.28	1.2 ± 0.1	6.0 ± 0.6
	35–40	0.39	0.73 ± 0.03	4.1 ± 0.4

(continued)

Table 3 (continued)

Plot	Layer depth, cm	ρ , g/cm ³	TOM, % of dry sample mass	A_U , Bq kg ⁻¹
S _{SL2}	0–5	0.19	11.0 ± 0.6	3.9 ± 0.4
	5–10	0.17	18.8 ± 0.9	4.5 ± 0.4
	10–15	0.42	6.4 ± 0.1	4.8 ± 0.4
	15–20	0.39	1.2 ± 0.1	5.9 ± 0.4
	20–25	0.36	0.63 ± 0.03	4.1 ± 0.4
	25–30	0.29	0.29 ± 0.02	3.2 ± 0.2
	30–35	0.33	0.31 ± 0.02	2.5 ± 0.3
	35–40	0.38	0.33 ± 0.03	2.8 ± 0.3
S _{SL3}	0–5	0.22	0.98 ± 0.05	3.9 ± 0.4
	5–10	0.12	1.3 ± 0.1	4.5 ± 0.4
	10–15	0.23	0.8 ± 0.1	4.8 ± 0.4
	15–20	0.18	1.6 ± 0.1	5.9 ± 0.4
	20–25	0.32	1.4 ± 0.2	4.1 ± 0.4
	25–30	0.30	1.4 ± 0.2	3.2 ± 0.2
	30–35	0.36	0.7 ± 0.1	2.5 ± 0.3
	35–40	0.27	0.6 ± 0.1	2.8 ± 0.3

Table 4 Inventories of ²³⁸U in the soil profiles (A_S)

Plot	A_S , Bq/m ²
SP _{S1}	2,633 ± 93
SP _{S2}	2,310 ± 120
P1	92.9 ± 4.9
S _{SL1}	883 ± 29
P2	674 ± 1723
S _{SL2}	476 ± 17
S _{SL3}	634 ± 22

The biggest inventory of uranium was found in the soils from SP_{S1} and SP_{S2} plots, which were located closer to Chernobyl NPP. Apparently, part of the uranium in these soils can be of Chernobyl origin.

As shown in Fig. 1, the character of the radionuclide distribution in two alluvial sod-podzolic sandy soils from the SP_{S1} and SP_{S2} plots differs markedly. In alluvial soil from the SP_{S1} plot, the biggest part of uranium was concentrated in the top (0–5)-cm layer and in soil from SP_{S2} plot—in (5–10)-cm layer. A longer period of excessive waterlogging of the SP_{S2} site compared to the SP_{S1} site probably contributes to the removal of uranium from the (0–5)-cm soil layer at SP_{S2} plot.

The peat-bog soil from P1 plot is characterized by a high content of organic matter (79–82% of dry soil mass). At this plot, 39 % of the total uranium inventories in the soil profile was in the (15–20)-cm layer, which may be due to the increase with depth of the proportion of humic acid components that bind uranium, with a commensurate total content of organic material.

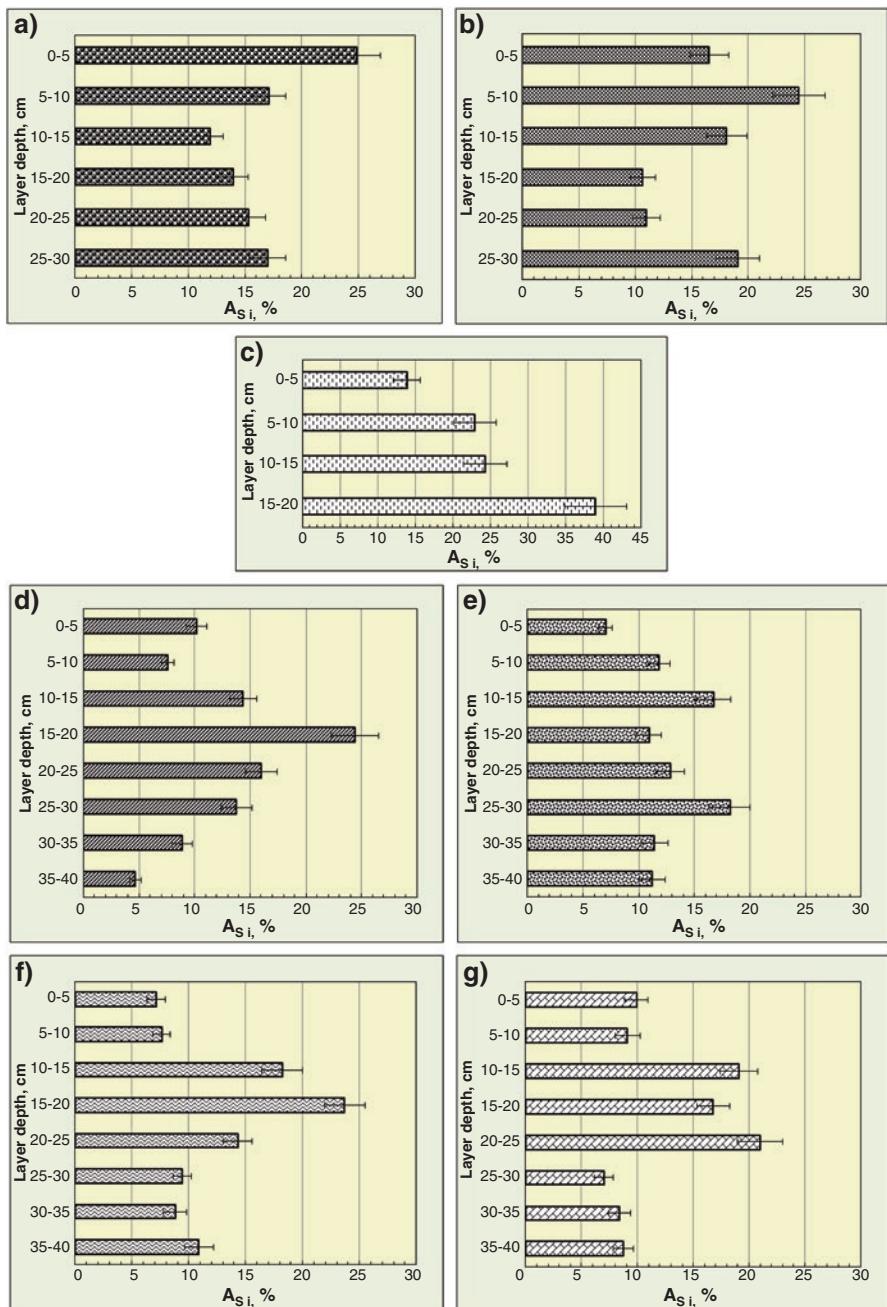


Fig. 1 Vertical distribution of ^{238}U in soils: (a) SP_{S1}; (b) SP_{S2}; (c) P1; (d) S_{SL1}; (e) P2; (f) S_{SL2}; (g) S_{SL3} ($A_{S,i}$, % of radionuclide inventory in the soil profile)

In all sod-gley soils ($S_{SL}1$, $S_{SL}2$ and $S_{SL}3$ plots), there was an increase in the share of uranium at a depth (10–25)-cm from the soil surface as compared to above and below the underlying layers. The observed differences in the distribution of uranium in soddy-gley soils can be due to the different composition of the underlying rocks on which soils are formed.

In the distribution of uranium along the vertical profile of the alluvial peaty-gley soil (P2 plot), two maxima are observed at a depth of (10–15) and (25–30) cm. At $S_{SL}1$, $S_{SL}2$, $S_{SL}3$, and P2, plots (0–5) and (5–10)-cm soil layers are depleted in uranium compared to (10–15)-cm soil layers, which may be due to the removal of uranium during the flood periods, as well as with the assimilation of radionuclides by plant organisms.

In general, the distribution of uranium along the vertical profiles of the studied soils, as in the case of natural uranium inherited from soil-forming rocks, depends on the genetic features and water regime of soils (Aleksahin et al. 1990, Morton et al. 2002; Titayeva 2005; Anisova and Yakushev 2008). Along with the accumulation of uranium in the upper organic layer enriched with organic matter (SP_S1 and SP_S2 plots), a relatively uniform vertical distribution of uranium (plot P2), an increase in its content with depth (plot P1), and accumulation in deeper layers of soil ($S_{SL}1$, $S_{SL}2$, and $S_{SL}3$ plots) were observed. In all cases considered, in the (0–20)-cm layer, 46–57% of the uranium inventory in the soil profile was concentrated.

5 Speciation Uranium in Soils and K_d Coefficient

5.1 *Uranium in the Interstitial (Pore) Waters of Soils*

During the migration of radionuclides from soil to vegetation, groundwater and surface water, soil pore waters play an important role. Pore waters are found mainly in small (less than 2 mm in diameter) soil capillaries and are retained by interaction with the surface of soil particles. Only some natural soils with a high content of clay fraction (e.g., clay soils) can contain larger closed pores, where part of the pore moisture is in a free state. In such pores, water molecules that are sufficiently far from the surface of soil particles practically do not experience its influence, and when the pores are opened, part of the water flows freely out of the soil under the action of gravity. The possible presence of such free soil moisture pore waters differ from the liquid phase of the soil. However, in practically all soils, the main part of the pore moisture is in a bound state and forms the liquid phase of the soil complex.

Pore waters of soils are open thermodynamic systems, genetically related to the solid phase of the soil complex and other types of natural waters. The pore moisture is constantly in contact with the solid phase and contains elements (including uranium) in the most mobile (migratory-active) state. In the presence of a difference in chemical potentials, the components of soil pore solutions can pass into ground and surface waters and thus participate in the geochemical migration of elements. Chemical elements in the forms present in the pore waters of soils can be actively included in the

processes of biological migration, since mainly from this kind of soil solutions plants assimilate the elements of mineral nutrition and together with them absorb the radionuclides from the soil (Ovsiannikova et al. 2000; Rachkova et al. 2010).

The radionuclide redistribution in ecosystems and their entry into the human body depend often on the content of radionuclides in soil pore waters; therefore, this indicator is among the most important factors determining the dose loads of the population. The samples of (0–10)-cm layers of soils for obtaining the pore solutions were sampled in 2007–2010. Location and soil type of sampling sites, content of total organic matter (TOM), water capacity (WC), acidity (pH_{KCl}), and concentration activity of ^{238}U (A_{U}) in the soil samples are presented in Table 5.

The sampling sites were located far from anthropogenic sources of uranium and at the distance of ~50 km and more from ChNNP. Presumably, uranium in the soils from these sites was mainly of natural origin. The soil samples were represented by sod-podzol sandy (SP_{S3}-SP_{S10} plots), sandy loam (SP_{SL3}-SP_{SL10} plots) and loamy (SP_{L1}-SP_{L3} plots), alluvial sod loamy (S_{L1}, S_{L2}, S_{L3} plots), peaty-gley (P3 plot), peat-bog (P4, P6 plots), and highly mineralized peaty (P5 plot) soils.

The samples of mineral soils of different granulometric compositions (sandy, sandy loam, and loamy) differed markedly in the content of the “physical clay” fraction (less than 1×1^{-5} m), the organic matter, the water capacity (WC), and the acidity. The total organic matter content (TOM) in samples of sandy and sandy loam mineral soils was 1.8–3.4%, and in samples of loamy soils—4.0–8.5%. The content of organic matter in samples of organic soils was in the range of 21.7–76.6% of the mass of dry soil. Water capacity of mineral sandy and sandy loam soils varied within 26.2–38.1%; loamy, 47.1–91.0%; and organic, 114–550% of mass of absolutely dry soil. High water capacity (more than 500% of the mass of the solid phase of the soil) is characteristic for samples of peat-bog soils containing 68–77% total organic matter of the mass of absolutely dry samples (P3 and P4 plots). The lower water capacity (114–190%) is characterized by samples of peaty (P5 plot) and peaty-gley (P6 plot) soils with TOM 21.7 and 60.4% accordingly. This means that sandy and sandy loam soil are capable of retaining 0.26–0.38 kg pore water; loamy soils, 0.47–0.52 kg; and organic soils, 1.1–5.5 kg per 1 kg of solid soil phase.

Soil content of ^{238}U of 4.8–19.8 Bq kg^{-1} (Table 5) corresponds to a radionuclide concentration of (0.39–1.59) mg kg^{-1} or $(3.9\text{--}15.9) \times 10^{-5}$ wt. %; activity concentration of ^{238}U in soil pore solution was (0.002–0.056) Bq kg^{-1} (Table 6).

The portions of ^{238}U in the soil pore solutions of the total radionuclide in the correspondent soil samples are shown in Fig. 2.

In mineral soils, the portion of ^{238}U in the pore solutions was within 0.036–0.19% of the total uranium content in the soil samples, and the fraction of uranium in pore solution increased from loamy soils (0.036–0.072%) to sandy loamy (0.063–0.087%) and to sandy (0.10–0.19%) soils (Fig. 2a, b, c).

In organic soils (Fig. 2d), the fraction of ^{238}U in the pore solution varied in the range 0.12–1.3%, but in most cases, it was within 0.1–0.2%. In the most species of peat-bog and sod-podzolic sandy soils, the portions of uranium in the composition of pore solutions were commensurable.

Table 5 Location and soil type of sampling sites, content of total organic matter (TOM), water capacity (WC), pH_{KCl}, and concentration activity of ²³⁸U (A_U) in the soil samples

Plot	Nearest settlement, geographical coordinates	TOM, %	WC, %	pH _{KCl}	A_U , Bq kg ⁻¹
<i>Sod-podzolic sandy soils</i>					
SP _S 3	Yelsk, Yelsk district Gomel region 51°28'56" N; 30°34'57" E	2.1	29.9	4.5	10.1 ± 0.8
SP _S 4	Slovechno, Yelsk district Gomel region 51°37'55" N; 29°04'06" E	3.4	35.2	4.5	5.1 ± 0.4
SP _S 5	Boriskovichi Mozyr' district Gomel region 52°02'60" N; 29°07'60" E	1.8	28.6	4.4	7.3 ± 0.5
SP _S 6	Khoiniiki, Khoiniiki district Gomel region 51°53'18" N; 29°57'44" E	1.9	31.3	4.6	5.2 ± 30.4
SP _S 7	Novoselki, Khoiniiki district Gomel region 51°49'00" N; 29°52'00" E	2.7	30.9	4.6	7.5 ± 0.6
SP _S 8	Kommunar, Buda Koshelev district Gomel region 52°38'07" N; 30°49'38" E	2.7	38.1	4.9	6.8 ± 0.5
SP _S 9	Komarin, Brahin district Gomel region 51°28'56" N; 30°34'57" E	3.2	29.2	5.3	4.8 ± 0.4
SP _S 10	Petritskoye, Brahin district Gomel region 51°53'50" N; 30°23'50" E	1.9	26.2	4.6	7.7 ± 0.6
<i>Sod-podzolic sandy loam soils</i>					
SP _{SL} 1	Zhuky, Yelsk district Gomel region 51°44'18" N; 28°58'04" E	1.9	29.9	4.6	6.5 ± 0.4
SP _{SL} 2	Skorodnoye, Yelsk district Gomel region 51°37'38" N; 28°49'17" E	2.6	32.8	5.5	8.4 ± 0.7
SP _{SL} 3	Bobrovniiki, Ostrovets district Grodno region 54°43'60" N; 26°04'00" E	2.8	33.1	5.4	8.6 ± 0.7
SP _{SL} 4	Chirkovichi, Svetlogorsk district Gomel region 52°39'45" N; 29°38'50" E	3.0	33.6	4.7	6.2 ± 0.5
SP _{SL} 5	Zhlobin, Zhlobin district Gomel region 52°53'13" N; 30°04'03" E	2.4	27.6	5.2	9.8 ± 0.7
SP _{SL} 6	Rogachev, Rogachev district Gomel region 53°05'29" N; 30°03'12" E	3.1	31.2	5.2	10.6 ± 0.8
SP _{SL} 7	Dovsk, Rogachev district Gomel region 53°09'28" N; 30°27'52" E	2.3	26.9	4.9	7.6 ± 0.6
SP _{SL} 8	Dyatlovo, Dyatlovo district Grodno region 53°28'00" N; 25°23'60" E	2.0	31.1	5.2	6.4 ± 0.5
SP _{SL} 9	"Radon" sanatorium, Dzyatlava district Grodno region 53°31'05" N; 25°30'43" E	2.2	31.6	4.7	7.7 ± 0.6
SP _{SL} 10	Porechye, Porechye district Grodno region 53°52'26,9" N; 24°09'02,3" E	1.9	28.4	4.5	10.0 ± 0.7
<i>Sod and sod-podzolic loamy</i>					
SP _L 1	Homsk, Drogichin district Brest region 52°19'60" N; 25°13'60" E	6.2	47.1	6.4	11.5 ± 0.8

(continued)

Table 5 (continued)

Plot	Nearest settlement, geographical coordinates	TOM, %	WC, %	pH _{KCl}	A _U , Bq kg ⁻¹
SP _L 2	Anusino, Minsk district Minsk region 54°02'13.4" N; 27°11'05.9" E	4.0	50.6	6.9	19.8 ± 1.3
SP _L 3	Lozoviyе, Ostrovets district Grodno region 54°47'04" N; 26°13'02" E	5.0	49.6	5.7	13.0 ± 1.0
S _L 1	Dovlyady, Narovlya district Gomel region 51°31'26" N; 30°03'16" E	8.5	91.0	6.6	12.0 ± 0.8
S _L 2	Drisvyaty, Braslav district Vitebsk region 55°34'60" N; 26°40'60" E	5.3	52.1	6.3	9.4 ± 0.8
S _L 3	Sharkovschina, Vitebsk region 55°21'13" N; 27°29'07" E	8.0	67.0	6.3	11.1 ± 0.8
<i>Organic soils</i>					
P3	Mikashevichi, Luninets district Brest region 52°14'46" N; 27°26'32" E	76.6	550	4.3	6.1 ± 0.4
P4	Besed' Vetka district Gomel region 52°37'60" N; 31°13'00" E	68.4	530	5.9	6.4 ± 0.4
P5	East edge of Minsk (Minsk region) 53°49'50" N; 27°39'50" E	21.7	114	5.4	18.0 ± 1.6
P6	Zhodishki Smargon' district Grodno region 54°37'00" N; 26°26'60" E	60.4	190	5.7	11.2 ± 0.8

Differences in the content of uranium in the pore waters of soils were due to the peculiarities of the structure of the sorption soil complex: different ratios of granulometric fractions and the content and composition of mineral and organic components, acidity, moisture capacity, and other properties that affect the release of radionuclides into pore waters. A close correlation was found between the content of uranium ($\alpha_U, \%$) and organic components ($OM_{sol}, \%$) in pore solutions of mineral soils (Fig. 3).

Uranium is characterized by a high tendency to complex formation (Sheppard and Campbell 1980; Katz et al. 1991). In soil solutions and other types of natural waters, it can be present simultaneously in the form of anionic, cationic, and neutral (molecular) complex compounds with organic and inorganic ligands (Katz et al. 1991). Under natural conditions, the main part of organic material of soils is in the solid phase. Even in cases where the fraction of fulvic acids (FA) exceeds the humic acids (HA) fraction, most of the FA soluble in the free state is associated in soils with high-molecular-weight poorly soluble HA and with the mineral part of the absorbing soil complex (Titayeva and Taskayev 1983; Zhang et al. 1997). Only a small part of relatively low-molecular organic components enters the pore waters of soils. The presence of a correlation between the content of uranium and organic components in the porous waters of soils indicates that the entry of uranium into soil water is most likely realized as complex compounds with organic constitu-

Table 6 Activity concentration of ^{238}U in the soil pore solutions (A_{solution}) and the percentages of organic matter (b_{OM}) in the solutions of their total content in the soil samples

Plot	Soil	$A_{\text{solution}}, \text{Bq kg}^{-1}$	$b_{\text{OM}}, \%$
SP _{S3}	Sod-podzolic sandy	0.056 ± 0.009	0.171 ± 0.009
SP _{S4}	Sod-podzolic sandy	0.027 ± 0.004	0.210 ± 0.010
SP _{S5}	Sod-podzolic sandy	0.044 ± 0.006	0.188 ± 0.009
SP _{S6}	Sod-podzolic sandy	0.026 ± 0.004	0.171 ± 0.009
SP _{S7}	Sod-podzolic sandy	0.043 ± 0.006	0.210 ± 0.010
SP _{S8}	Sod-podzolic sandy	0.026 ± 0.003	0.130 ± 0.008
SP _{S9}	Sod-podzolic sandy	$0.017 \pm 0.002_1$	0.123 ± 0.007
SP _{S10}	Sod-podzolic sandy	0.038 ± 0.005	0.118 ± 0.007
SP _{SL1}	Sod-podzolic sandy loam	$0.018 \pm 0.003_{18.3}$	0.071 ± 0.009
SP _{SL2}	Sod-podzolic sandy loam	$0.017 \pm 0.003_{18.5}$	0.070 ± 0.006
SP _{SL3}	Sod-podzolic sandy loam	$0.018 \pm 0.003_{17.4}$	0.093 ± 0.007
SP _{SL4}	Sod-podzolic sandy loam	$0.016 \pm 0.003_{16.4}$	0.076 ± 0.006
SP _{SL5}	Sod-podzolic sandy loam	0.021 ± 0.003	0.072 ± 0.006
SP _{SL6}	Sod-podzolic sandy loam	0.022 ± 0.004	0.078 ± 0.006
SP _{SL7}	Sod-podzolic sandy loam	0.019 ± 0.003	0.073 ± 0.006
SP _{SL8}	Sod-podzolic sandy loam	0.013 ± 0.002	0.061 ± 0.006
SP _{SL9}	Sod-podzolic sandy loam	0.017 ± 0.003	0.093 ± 0.007
SP _{SL10}	Sod-podzolic sandy loam	0.028 ± 0.005	0.076 ± 0.006
SP _{L1}	Sod-podzolic loamy	0.011 ± 0.002	0.040 ± 0.004
SP _{L2}	Sod-podzolic loamy	0.014 ± 0.002	0.040 ± 0.004
SP _{L3}	Sod-podzolic loamy	0.018 ± 0.003	0.077 ± 0.006
S _{L1}	Alluvial sod loamy	0.009 ± 0.002	0.077 ± 0.006
S _{L2}	Alluvial sod loamy	0.011 ± 0.002	0.074 ± 0.006
S _{L3}	Alluvial sod loamy	0.012 ± 0.002	0.070 ± 0.006
P3	Peaty-gley	0.014 ± 0.002	2.1 ± 0.1
P4	Peat-bog	0.0023 ± 0.0004	0.33 ± 0.02
P5	Highly mineralized peaty	0.023 ± 0.003	0.26 ± 0.2
P6	Peat-bog	0.007 ± 0.001	0.21 ± 0.01

ents of soils. At pH more than 7.5, uranium can also enter the soil water in the form of bi- and tricarbonate uranyl complexes: $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ (Katz et al. 1991).

Earlier, it was shown that FA with a molecular mass of 700 D and less predominates in the composition of FA of soil pore solutions. In the HA composition, compounds with a molecular mass of 2400 D were found predominantly. The fraction of HA components, as a rule, did not exceed 10% of the mass of organic material of pore waters (Sokolik et al. 2002).

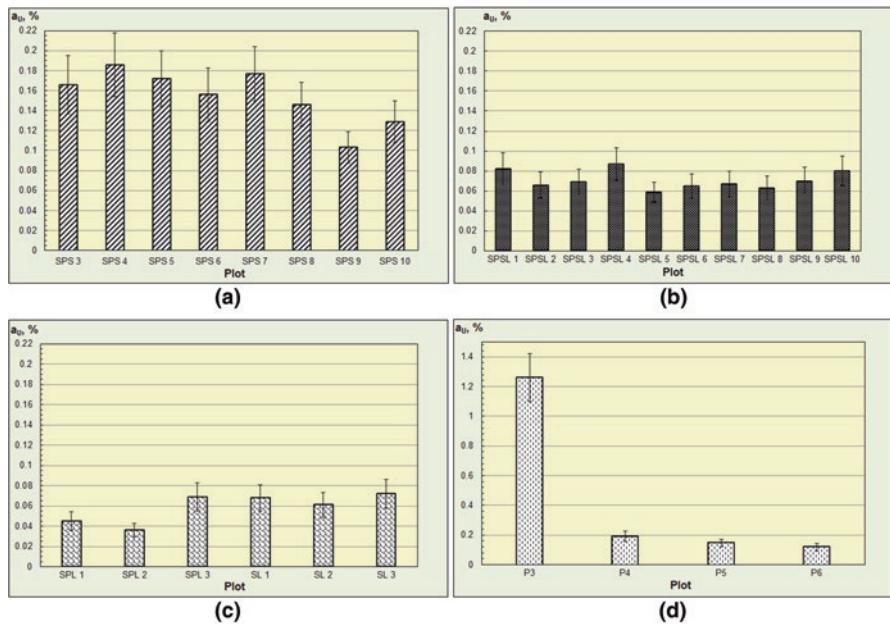


Fig. 2 The portions of uranium in pore solutions of water-saturated soils (a_{U} , % of its total content in the soil samples): (a) sod-podzolic sandy; (b) sod-podzolic sandy loam; (c) sod-podzolic and sod loamy soils; (d) organic soils

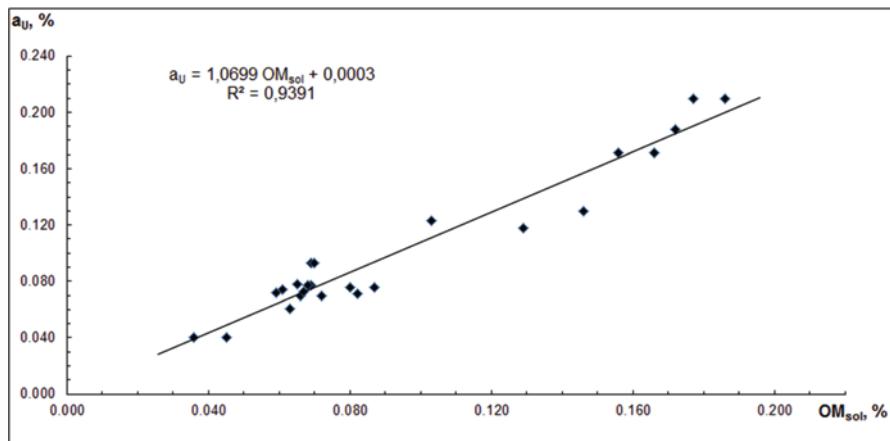


Fig. 3 The relation between portions of ^{238}U (a_{U} , %) and organic matter (OM_{sol} , %) in the pore solution of water-saturated mineral soils

5.2 Reversibly Bound (Exchangeable) and Mobile (Conditionally Biologically Available) Uranium in the Soils

Uranium reversibly associated with components of the sorption complex of soil is in potentially mobile (exchangeable) form. These can be cationic, anionic, and neutral (molecular) uranium complexes with organic and inorganic components of the soil, as well as soluble hydrolysis products that are capable of entering soil solution. The composition and ratio of these forms of uranium depends on the redox conditions, the pH of the medium, and the presence of complexing addends (Sheppard and Campbell 1980; Katz et al. 1991; Rachkova et al. 2010). In the upper well-aerated horizons of soils, as a rule, an oxidizing environment is formed; therefore, uranium, as a rule, is in the degree of oxidation +6. In this case, reversibly bound uranium could be presented of UO_2^{2+} , its complex compounds, and hydrolytic forms of U (VI), (UO_2OH^+) , $\text{UO}_2(\text{OH})_2^0$, $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_4^{2-}$, etc.), which can be found in the soil waters (Katz et al. 1991; Sparovek et al. 2002; Rachkova et al. 2010).

Reversibly bound (exchangeable) uranium is distributed between the solid phase and the pore solution of the soil until interphase equilibrium is established. However, the bulk of reversibly bound uranium remains in the solid phase of the soil. In redistribution of uranium along the soil profile and the assimilation by vegetation through the root systems, its content in the soil pore solution decreases, and the equilibrium distribution of the element between the solid phase and the pore solution of the soil is disturbed. Restoration of the disturbed equilibrium is carried out by transition from a solid phase to a solution of uranium, reversibly connected with components of the soil complex (exchangeable form). The reserve of uranium in pore solutions at the soil boundary with the root system of the plant can be supplemented additionally by uranium more firmly associated with the components of the soil complex and entering the aqueous phase of the soil under conditions of increased acidity. Such conditions are formed by the plant in the process of assimilation of nutrients (Grodzinsky 1989). Elements entering the soil solution at the border with the root system of plants are in a form that can be called mobile or conditionally biologically available.

The relative quantity of uranium associated with reversibly bound fraction in the soil samples is presented in Fig. 4.

In the soil samples studied, the uranium content in the exchange form (U_{exch}) was within the range of 0.1–2.9% of the total uranium content in the soil. The minimum portion of U_{exch} (0.10–0.33%) is found in loamy soils and the maximum in sandy soils (1.5–2.9%). Sandy loam soils contain an intermediate position between them in the content of exchangeable uranium (0.8–1.6%). In organic soils portion of exchangeable uranium was within the range of 0.7–2.6%. The minimum content of U_{exch} is characteristic of peat-bog soil with relatively low mass fraction OM_{sol} (~0.2%, P4 plot), and the maximum content of U_{exch} was found in peat-bog soil with a relatively high mass fraction of OM_{sol} (2.1%, P3 plot).

The relative quantity of uranium associated with mobile (conditionally biologically available) fraction (U_{mob}) in the soil samples is presented in Fig. 5.

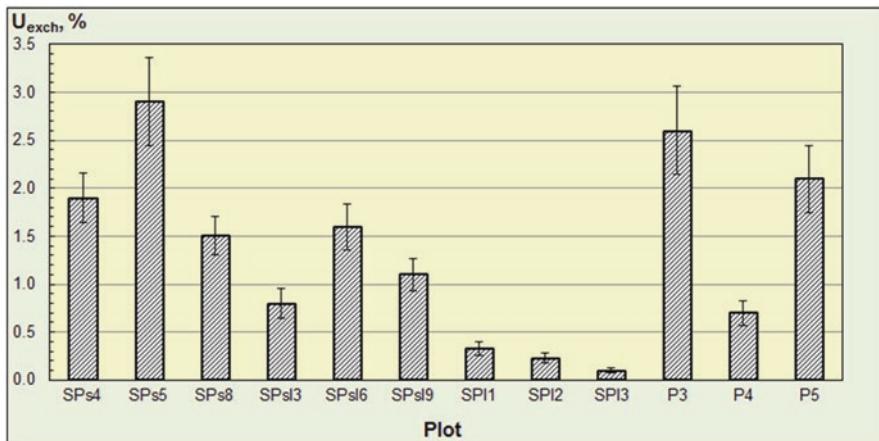


Fig. 4 The portions of exchangeable uranium in the soil samples (U_{exch} , %)

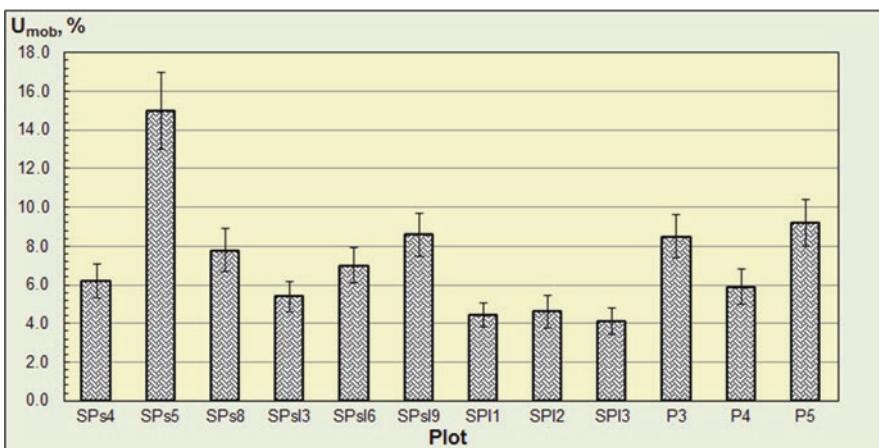


Fig. 5 The portions of mobile (conditionally biologically available) uranium in the soil samples (U_{mob} , %)

In mineral soils, the content of U_{mob} varied in the range 4.1–15% of the total uranium content in the soils. As in the case of U_{exch}, the lowest portions of U_{mob} (4.1–4.6%) were found in loamy soils and the highest (6.2–15%) in sandy soils. The sandy loam soils with portion of U_{mob} 0.8–1.6% occupied intermediate position between the loamy and the sandy soils.

In organic soils portion of U_{mob} were 5.9–9.2%. The lowest portions of U_{mob} were found in peat-bog soil from P4 plot and maximum in peat-bog soil from P3 plot. These soils differed significantly in the content of organic components in soil pore solutions (OM_{sol}). Portion of OM_{sol} in the soil from the P4 plot was ~0.2 wt. % and in the soil from the P3 plot 2.1 wt. %.

In both mineral and organic soils, portions of U_{exch} and U_{mob} , as a rule, considerably exceeded the portions of uranium in pore solutions. The obtained data indicate the presence in the solid phase of soils of a significant reserve of reversibly sorbed uranium capable of entering the pore solutions and being included in biogeochemical migration of uranium in terrestrial ecosystems. The uranium remaining in the solid phase of the soil complex (in this case, not passing into a solution of 1 M HCl) is in the soil in a fixed form. The relative quantity of uranium associated with fixed fraction (U_{fix}) in the soil samples is shown in Fig. 6.

As can be seen from the obtained data, in the soils widely distributed in Belarus, the main amount of uranium (85–96%) is in fixed form.

In general, in the studied soils, the portion of uranium in the mobile (conditionally biologically available) form did not exceed 15% of the total uranium content in soil samples. According to the authors of the work (Vandenhove et al. 2014), in natural and anthropogenic affected soils with different contamination histories and uranium concentration, portion of U_{exch} was in the range of ≤ 2 –19.7, and portion of uranium associated with exchangeable and acid soluble fraction (corresponding in our case to a mobile form) was in the range of 0.3–13.7%. Our data on the content of uranium in appropriate forms are in good agreement with these results.

In the same time, in semi-hydromorphic and hydromorphic soils of the Southern Urals (in the area of the Itkul and Sinara lakes), which have been subjected to anthropogenic impact, the portions of uranium in mobile form reached 90% (Poludin et al. 2013). According to the Vodyanitskiy and Bol'shakov (1998), the presence of uranium in mobile form in excess of 20–30% of its total content in soil unambiguously indicates the technogenic contamination of the soil with uranium.

The higher percentages of U_{exch} and U_{mob} in sandy soils compared to loamy soils are in accord with the higher uptake of uranium by plants. The uptake of uranium is generally higher on sandy soils compared to loamy soils (Sheppard and Evenden 1988; Mortvedt 1994; Vandenhove et al. 2009).

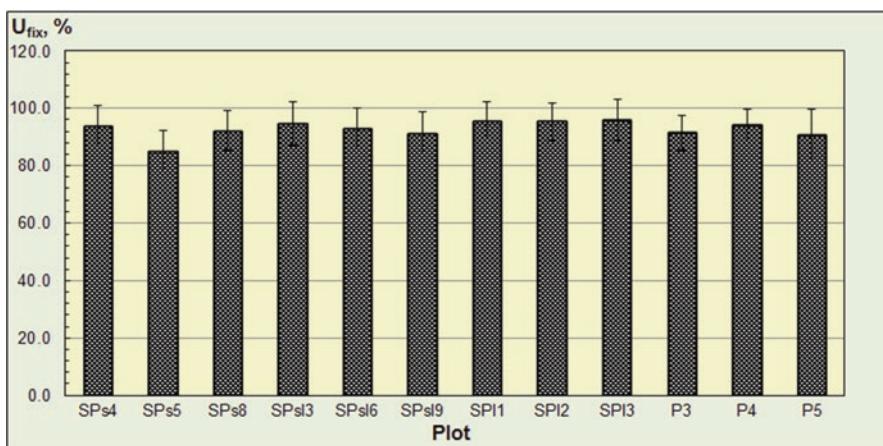


Fig. 6 Portions of fixed uranium (U_{fix} , %) in the soil samples

5.3 The “Solid Phase-Pore Solution” Distribution Coefficient in Soil (K_d)

K_d coefficient is the ratio between activity concentrations of radionuclide in the solid phase and pore solution of soil in the state of interphase equilibrium or near it:

$$K_d = \text{Error}!, \quad (1)$$

where $A_{\text{solid phase}}$ and A_{solution} are activity concentrations of ^{238}U in solid phase and pore solution after 3 weeks of moistening the calculated amount of distilled water to the state of water saturation.

Taking into account the activity concentration of ^{238}U in the soil sample taken for the preparation of pore solution and its water capacity (WC), the activity concentration of ^{238}U in the solid phase of the soil can be estimated, using formula (2):

$$K_d = \text{Error}!, \quad (2)$$

where A_U (Bq kg^{-1}), activity concentration of ^{238}U in absolutely dry soil; A_{solution} (Bq kg^{-1}), activity concentration of ^{238}U in soil pore solution; and WC (%), water capacity of the soil.

The activity of uranium in water-saturated soil containing m kg of solid phase is equal to $A_U \times M_{\text{solid}}$, where M_{solid} is mass of solid phase of soil.

In the state of interphase equilibrium

$$A_{\text{solid phase}} = \text{Error}!, \quad (3)$$

where M_{solution} is mass of soil pore solution,

$$M_{\text{solution}} = 0.01WC \times M_{\text{solid}} \quad (4)$$

then

$$K_d = \text{Error} = \text{Error}! \quad (5)$$

The K_d coefficient can be considered as a parameter characterizing the soil's ability to prevent redistribution of the radionuclide in terrestrial ecosystems. As the coefficient K_d increases, the soil's barrier functions become stronger, and, accordingly, the mobility of the element in the soil decreases (Iskra and Bakhurov 1981).

The K_d coefficients for ^{238}U in the (0–10)-cm layer of water-saturated soils are given in Fig. 7.

As it is seen from the data received, the genetic type of soil significantly affected the value of the K_d coefficient. Among the mineral soils, the minimum coefficients K_d (166–282; average, 207; coefficient of variation, 20) were characteristic of sandy

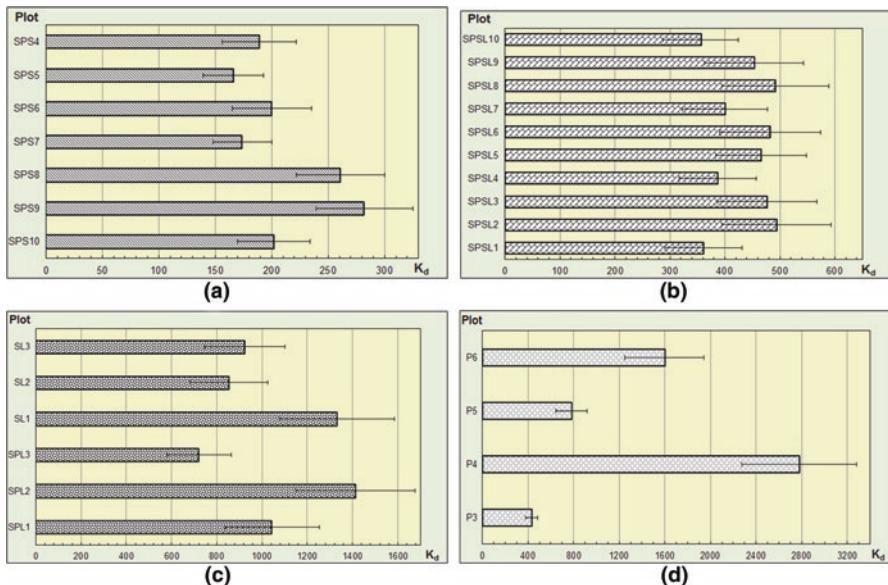


Fig. 7 Distribution coefficient (K_d) of ^{238}U between solid phase and pore solution of water-saturated soils: (a) sod-podzolic sandy; (b) sod-podzolic sandy loam; (c) sod-podzolic and sod loamy; (d) organic

soils. The maximum coefficients K_d (720–1,400; average, 1050; coefficient of variation, 260) were found for loamy soils. The coefficient K_d for sandy loamy soils (360–490; average, 437; the coefficient of variation, 13) occupied an intermediate position between sandy and loamy soils. This means that the sorption capacity of mineral soils with respect to uranium increased with the transition from sandy soils to sandy loams and then to loamy soils.

The fixation of uranium by soils can be explained with sorption by fine soil material, interaction with organic matter, the inclusion of uranium into composition of iron (III) oxides and hydroxides, and the formation of oxalates, phosphates, and other difficultly soluble compounds with components of the soil complex (Iskra and Bakhurov 1981).

The relatively high sorption properties of loamy soils with respect to uranium are largely due to the high (20–40 wt. %) content of the “physical” clay (the granulometric fraction with a particle size of less than 1×10^{-5} m). In loamy soils, the content of this fraction was 20–40 wt. %, in sandy loam—10–20%, and in sandy soils—no more than 10% (Gorbilyova 2007).

The samples of loamy soils were also characterized by a lower acidity (pH_{KCl} —5.7–6.6) compared to samples of sandy and sandy loamy soils (pH_{KCl} —4.4–5.5) (Table 5).

Consequently, among the mineral soils considered, the best geochemical barrier preventing the redistribution of uranium in the soil was the loamy soils. They can be surpassed only by clay soils with the higher clay content.

In organic soils, the K_d coefficient varied over a wider range (430–2.780) than in mineral soils. The sorption capacity of these soils with respect to uranium increased in the following order: peat-bog soil from P3 plot—peaty soil from P5 plot—peaty-gley soil from P6 plot—peat-bog soil from P4 plot.

The organic soils differed significantly in the content and structure of organic components, water capacity, and acidity. In the different species of peat-bog soils, content of organic matter varied in the range of 21.7–76.6 wt. %, the value of water capacity, 114–550 wt. %; and pH_{KCl} , in the range of 4.3–5.9.

In general, the most species of peat-bog soils had a high sorption capacity with respect to uranium. The processes of hydrolysis and formation of complex uranium compounds with organic and inorganic constituents of the soil have a significant effect on the ability of soils to fix uranium.

In organic soils, the fixation of uranium significantly depended on the ratio of soluble and hardly soluble organic and organomineral components and the acidity of the soil medium. An increase in the portion of hardly soluble organic and organomineral components in the organic matter of the soil and a decrease in the acidity of the soil medium can explain the increase in the value of K_d coefficient in the aforementioned series of peat-bog type soils, which indicated an increase in the degree of fixation of uranium in this order (Sokolik et al. 2010).

The sorption properties of the soils of the peat-bog type basically determine high-molecular-weight HA. In soils, most of the FA is usually associated with high-molecular-weight HA and the mineral part of the sorption soil complex (Ponomareva and Plotnikova 1980; Sokolik et al. 2002). Only a small part (0.2–2.1%) of the total organic matter of the soil enters the soil pore waters (Table 6). Basically, these are relatively low-molecular-weight organic components, with which uranium is able to form complex compounds (Katz et al. 1991; Sparovek et al. 2002).

The fixation of the main part of uranium by an organomineral complex of soils limits its distribution in the soil and its entry into groundwater and vegetation. However, the barrier functions of soils also depend on the depth of groundwater, the degree of soil moistening, and the intensity of the redistribution of moisture along the soil profile (Titayeva and Taskayev 1983).

With excessive soil moistening under anaerobic conditions, the content of mobile forms of iron increases as a result of the reduction of Fe (III) to Fe (II), which can lead to a decrease in the degree of fixation of uranium in soils (Nikolayeva and Yeremina 2001; Luo and Gu 2009).

The obtained information on the content of uranium in the migratory-active, exchangeable, and mobile (conventionally biologically accessible) forms in the soils, as well as on the values of the uranium distribution coefficient between the solid phase and the porous soil solution, can be used for parametrization of models for forecasting the redistribution of uranium in soil media and pollution levels of natural waters and biological communities.

6 Effect of Temperature on Uranium Mobile Species in the Soils

The objects of the study were samples (0–20)-cm of soils of sod-podzolic light loamy (coarse sandy) and peaty lowland type, containing predominantly uranium of natural origin. Samples of soils were selected in the summer of 2016 in the Drogichinsky district of the Brest region and in the Minsk district of the Minsk region. The main characteristics of soil samples are given in Table 7.

The sample of organic soil (T) was more acidic than the sample of mineral soil (SP). The water capacity (WC), the content of organic components (TOM), mobile calcium (Ca_{mob}), and potassium (K_{mob}) in peaty soil were significantly higher than in sod-podzolic light loamy soil. The fraction of physical clay in the sod-podzolic soil was 24 wt. %.

In the soils, uranium isotopes ^{238}U , ^{235}U , and ^{234}U were present in the ratio by activity, which was practically not different from the natural one. The ratio of $^{238}\text{U}/^{234}\text{U}$ by activity was 1.0. The total activity of the uranium in the soil samples estimated by activities of ^{238}U and ^{234}U , as the contribution of ^{235}U to the total soil activity was insignificant. The total content of uranium in the sod-podzolic light loamy soil was three times greater than in the peaty soil.

In laboratory conditions, two series of experiments with the air-dry and the water-saturated soil samples were performed. The soil samples were held for three weeks at specified temperatures in the range from -18 to $+30$ °C. Humidity of soil samples was controlled by their weight. The content of U_{mob} in soils was established by the method of radiochemical analysis of soil extracts with acetate-ammonium buffer solution (pH 4.8). The soil samples were treated by an extracting solution after the soil temperature was adjusted to (20 ± 2) °C. The obtained extracts were passed through the paper filters "blue tape".

Change in the content of U_{mob} in air-dry soil samples at varying temperature conditions. In air-dry conditions in the temperature range from -18 to $+30$ °C, the U_{mob} content in sod-podzolic light loamy soil was in the range from (1.6 ± 0.2) to (2.7 ± 0.2) Bq kg^{-1} of solid matter, and in peaty soil—from (0.87 ± 0.10) to (3.0 ± 0.2) Bq kg^{-1} . Under these conditions, the portion of U_{mob} in the sod-podzolic soil varied in the interval from (4.6 ± 0.6) to $(7.4 \pm 0.7)\%$, and in peaty soil—from (7.5 ± 0.7) to $(26 \pm 3)\%$. The results of the change in the portion of U_{mob} in soils after their aging at various temperatures in the air-dry state are given in Fig. 8.

As can be seen from Fig. 8, in both soils the portion of U_{mob} increased with increasing temperature from -18 to $+15$ °C. In this interval in soddy-podzolic soil, the portion of U_{mob} increased by approximately 20% and in peaty soil more than twice. With a further rise in temperature to $+30$ °C, the portion of U_{mob} in soils decreased compared to the levels reached at $+15$ °C: in light loamy soil by 1.7 times and in peaty soil by more than 3 times. The increase in the content of U_{mob} in air-dry soils with increasing temperature from -18 to $+15$ °C can be explained by an increase in the intensity of ion-exchange processes at the boundary of the solid phase of 'the soil—the soil pore solution'. Reduction of their content in the soils with

Table 7 Characteristics of the soil samples

Soil	TOM, wt. %	WC, wt. %	pH _{KCl}	pH _{H₂O}	HW, wt. %	C _{a_{mob}} , Mg kg ⁻¹	K _{mob} , Mg kg ⁻¹	A _{ΣU} , Bq kg ⁻¹
Sod-podzolic light loamy	4.25 ± 0.06	46.8 ± 1.2	6.8	7.7	1.80 ± 0.06	183 ± 10	136.1 ± 1.1	34.4 ± 2.1
Peaty of lowland type	25.8 ± 0.8	105.4 ± 1.5	5.7	6.0	5.46 ± 0.12	664 ± 44	219.0 ± 9.2	11.6 ± 0.7

TOM total content of organic matter, WC water capacity, HW content of hydrosopic water in air dry soil samples, C_{a_{mob}} and K_{mob} content of mobile calcium and potassium in dry samples (100–105 °C), A_{ΣU} activity concentration of total uranium in dry soil samples

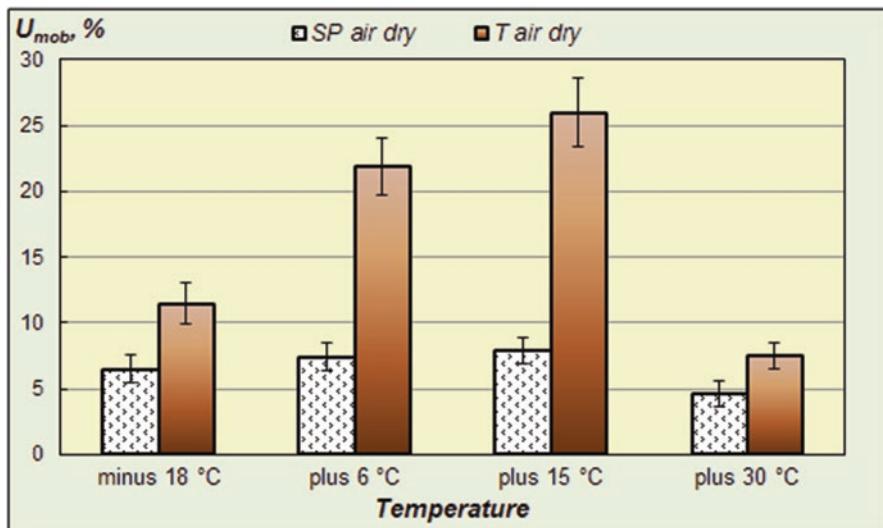


Fig. 8 The portions U_{mob} in air dry samples of sod-podzolic light loamy (SP) and peaty (T) soils after their aging at different temperatures

an increase in temperature from +15 to +30 °C could be caused by a change in the structure of the surface of soil aggregates, and to a greater extent was characteristic of peaty soil.

Change in the content of U_{mob} in water-saturated soil samples at varying temperature conditions. In the water-saturated sod-podzolic soil, the activity concentration of U_{mob} was in the range from (2.5 ± 0.2) to (0.9 ± 0.2) Bq kg⁻¹ of solid matter, and the fraction of U_{mob} was from (7.2 ± 0.7) to $(2.6 \pm 0.4)\%$ of the total uranium content in the soil. In the water-saturated peaty soil, the activity concentration of U_{mob} varied from (0.64 ± 0.07) to (2.5 ± 0.2) Bq kg⁻¹, and the fraction of U_{mob} was from (22 ± 2) to $(5.5 \pm 0.7)\%$.

Data on the variation with the temperature of the fraction U_{mob} in soils in the temperature range from -18 to +30 °C are given in Fig. 9.

In both water-saturated soils, the fraction of U_{mob} decreased with increasing temperature in the entire studied temperature range (from -18 to 30 °C). In peaty soil, the portion of U_{mob} declined by a factor of 4, and in sod-podzolic light loam soil by a factor of 2.8.

The decrease with increasing temperature of the fraction of U_{mob} in water-saturated soils could be associated with a change in the oxidation-reduction conditions with increasing temperature as a result of a decrease in the oxygen content in the water-filled soil pore space. Under these conditions, partial reduction of U (VI) to U (IV) by humic substances of the soil was possible. The degree of reduction could increase with increasing temperature. The compounds of U (IV) have a lower solubility in water than U (VI) compounds, which could be the reason for the

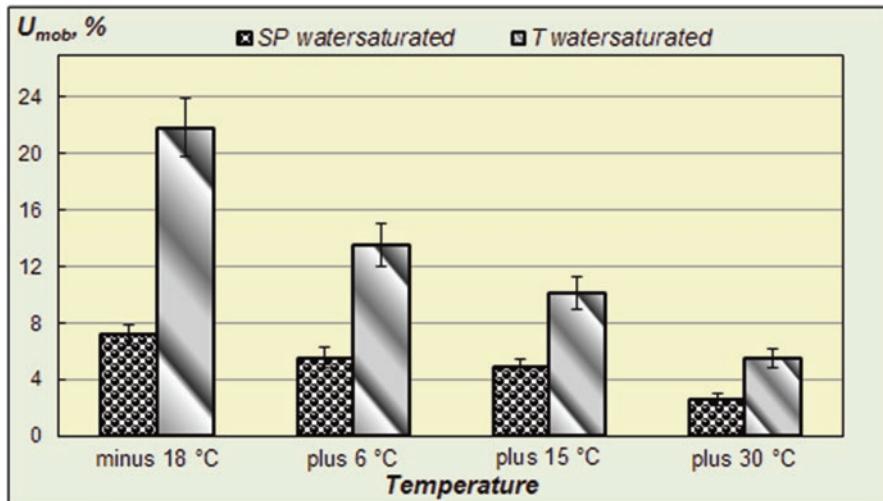


Fig. 9 The portions U_{mob} in water-saturated samples of sod-podzolic light loamy (SP) and peaty (T) soils after their aging at different temperatures

decrease in U_{mob} content with increasing temperature in conditions of water saturation of soils (Hanson ed. 1985; Titayeva 2005; Vodyanitskiy 2011). Another possible reason for the decrease in the content of U_{mob} in the soils could be associated with an increase in the degree of hydrolysis of U (IV) compounds with an increase in temperature, which led to an increase in the sorption of uranium by the solid phase of the soils.

In all the cases considered, the portion of U_{mob} in peaty soil was higher than in sod-podzolic light loamy soil. Most likely, this was due to the peculiarities of the chemical properties of uranium. The state and mobility of uranium is largely depends on redox conditions, the processes of complex formation and hydrolysis as well as on the solubility of the products formed. The reason for the increased portion of U_{mob} in peaty soil could be a higher acidity of this soil, which led to a lower degree of hydrolysis of uranium compounds than in the sod-podzolic soil, accompanied by the formation of poorly soluble products.

In general, the genetic type of soil significantly affects the proportion of U_{mob} in the soil, as well as the degree of change in uranium content in the mobile (conditionally biologically available) form as a function of temperature. In air-dry conditions, the maximum U_{mob} content in sod-podzolic light loamy and peaty soils was observed at a temperature of +15 °C. With a subsequent rise in temperature to + 30 °C, the content of U_{mob} in both soils was reduced.

In water-saturated soils, the maximum U_{mob} content was observed after soil freezing. Consequently, freezing during plant vegetation in conditions of increased soil moisture can increase the content of U_{mob} in soil, and increase uranium accumulation in plant products.

7 Effect of Humidity on Uranium Mobile Species in the Soil

The object of study was sod-podzolic soil, containing uranium mainly of natural origin. Soils of this type are widespread in the territory of Belarus. The soil was sampled in the summer of 2016 near the settlement Anusino, Minsk region. It was sampled by a metal drill to a depth of 20 cm from the soil surface using the “envelope method.” The soil characteristics are given in Table 8.

In the soil under consideration, the content of the fraction with a particle size of less than 1×10^{-5} m (physical clay) was 37 wt. %, which allowed it to be classified as medium loamy (silty-coarse dusty) soil. According to the $\text{pH}_{\text{H}_2\text{O}}$ (7.9), the soil was alkaline. In the soil, the ratio of $^{238}\text{U}/^{234}\text{U}$ by activity was 1.0. The total activity of the uranium in the soil estimated by activities of ^{238}U and ^{234}U isotopes.

The soil samples were moistened with distilled water to a predetermined level and held at a certain temperature for 3 weeks. After aging the soil samples under specified conditions, the uranium content in a mobile (conventionally biologically available) form (U_{mob}) was determined by chemical fractionation with subsequent radiochemical analysis of extracts. Extraction was carried out at a temperature of (20 ± 2) °C using an acetate-ammonium buffer solution (pH 4.8). The obtained extracts were passed through the paper filters “blue tape.”

Twelve series of experiments with samples of soils with humidity in the range of 5.5–140% of the WC were carried out. All experiments were performed in duplicate.

Change in the content of U_{mob} in the soil samples. U_{mob} content in the soil samples at humidity 5.5–140% of the WC depended on temperature conditions. For all soil moisture levels, the highest U_{mob} content was detected after soil freezing at a temperature of -18 °C, which was $1.98\text{--}2.79 \text{ Bq kg}^{-1}$ of dry soil ($0.080\text{--}0.112 \text{ mg kg}^{-1}$) or 5.6–7.9% of the total uranium content in the soil. After aging of soil at the temperature of $+15$ °C, content of U_{mob} in the soil was $1.76\text{--}2.64 \text{ Bq kg}^{-1}$ ($0.071\text{--}0.106 \text{ Bq kg}^{-1}$) of dry soil or 5.0–7.5% of the total uranium content and at the temperature of $+30$ °C— $1.14\text{--}1.78 \text{ Bq kg}^{-1}$ ($0.046\text{--}1.78 \text{ mg kg}^{-1}$) or 3.2–5.1%.

The change in the content of U_{mob} , depending on the moisture content in the soil samples, established for different temperature conditions, is shown in Fig. 10.

With good aeration in the upper layers of soils, an oxidative environment is usually formed, and under such conditions, uranium in the soil is in the oxidation state of +6. The mobile form of uranium can be represented by uranyl cations UO_2^{2+} and its complexes with organic acids of non-specific type (succinic, citric, malic, etc.).

Table 8 Characteristics of the soil

Soil	TOM, wt. %	WC, wt. %	pH_{KCl}	$\text{pH}_{\text{H}_2\text{O}}$	HW, wt. %	$\text{Ca}_{\text{mob}},$ Mg kg^{-1}	$\text{K}_{\text{mob}},$ Mg kg^{-1}	$A_{\Sigma\text{U}},$ Bq kg^{-1}
Sod-podzolic medium loamy	4.48 ± 0.09	50.6 ± 2.4	7.0	7.9	2.21 ± 0.08	500 ± 73	75.0 ± 4.9	35.2 ± 2.0

TOM total content of organic matter, *WC* water capacity, *HW* content of hydroscopic water in air dry soil samples, Ca_{mob} and K_{mob} content of mobile calcium and potassium in dry soil samples (100–105 °C), $A_{\Sigma\text{U}}$ activity concentration of total uranium in dry soil samples

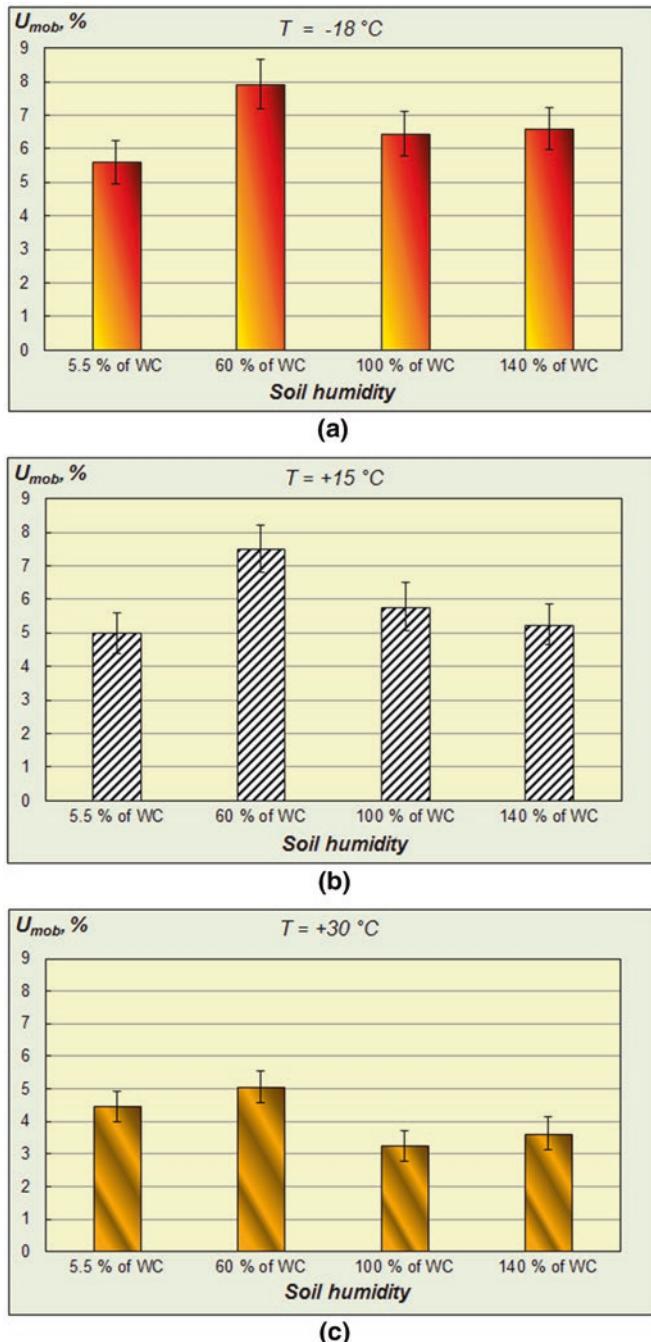


Fig. 10 Change of uranium fraction in the mobile form ($a_{U\text{ mob}}$, % of the total uranium content in the soil in dependence of the soil humidity after its aging at the temperature of: (a) -18 , (b) $+15$, (c) $+30$ $^{\circ}\text{C}$

relatively low-molecular humic acids and anions of mineral acids, for example, $[\text{UO}_2\text{Cl}]^+$, $[\text{UO}_2\text{Cl}_2]^0$, $[\text{UO}_2\text{SO}_4]^0$, etc. U_{mob} can also be represented by the simplest hydrolyzed forms of uranyl ($[\text{UO}_2\text{OH}]^+$, $[\text{UO}_2(\text{OH})_2]^0$, $[\text{UO}_2(\text{OH})_3]^-$) and their soluble complexes with soil components. In an acidic environment, the dominant form of uranium (VI) is UO_2^{2+} , complexes of hydroxides and phosphates are found in a neutral medium, and at a pH of 7.5 or more, uranium can also enter the soil waters in the form of bi- and tricarbonate uranyl complexes $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ (Sparovek et al. 2002; Diemann 2012).

As can be seen from the data presented in Fig. 10, for all the temperature regimes studied, the content of U_{mob} in the soil increased with an increase in soil moisture from 5.5 to 60% of the WC. A subsequent increase in soil moisture from 60 to 100% resulted in a decrease in the U_{mob} content, and the levels reached were practically preserved with a subsequent increase in humidity to 140% of the WC.

An increase in U_{mob} content with an increase in soil moisture from 5.5% to 60% could be due to an increase in the portion of water-soluble carbonate uranyl complexes that should be present in the soil under analysis ($\text{pH}_{\text{H}_2\text{O}}=7.9$). According to Chernykh and Prasanna (2000), an increase in soil moisture at a temperature above (10–15) °C leads to an increase in pH, which facilitates the dissolution of atmospheric carbon dioxide in the soil solution and the formation of water-soluble carbonate complexes. Reduction of U_{mob} content with increasing the soil moisture from 60% to 100% of the WC could be due to a change in oxidation-reduction conditions as a result of a decrease in the oxygen content when water filled the soil pore space. This led to the reduction of U (VI) to U (IV). Since U (IV) compounds have a lower solubility in water than U (VI) compounds, this could be the reason for the decrease in the content of U_{mob} with increasing soil moisture (Katz et al. 1991).

In addition, an increase in the pH of the soil medium with an increase in soil moisture from 60% to 100–140% of the WC increased the degree of hydrolysis of uranium compounds, which could contribute to the sorption of hydrolysis products by the components of the solid phase of the soil.

It should be noted that the content of U_{mob} in the soil samples subjected to freezing was higher than in the samples that were held at the temperature of +15 °C. This was observed at all levels of soil moisture, most notably for soil samples with a moisture content of 100% and 140% of the WC. From the data obtained, it follows that freezing the wet soil during the vegetation period can lead to an increase in U_{mob} content, which contributes to the accumulation of uranium by terrestrial ecosystem vegetation.

8 Conclusions

As a result analysis of the literature and our own experimental data, it was established that at present, there is uranium of natural and technogenic origin at the territory of Belarus. Technogenic uranium is mainly uranium of Chernobyl origin with an admixture of uranium of global fallout. Uranium of Chernobyl origin concentrated predominantly in the Polesie State Radiation Ecological Reserve. In the rest of the territory, there is mainly natural uranium, but use of mineral fertilizers,

dolomite flour, and other reclaiming additives in agriculture leads to additional amounts of uranium entering the soil. Initially, in the Chernobyl products falling on the territory of Belarus, uranium was mainly in the composition of oxidized fuel particles. Over time, the fuel particles were destroyed, and the uranium species changed as a result of interacting with the components of the environment and gradually approached to the natural uranium species.

The distribution of uranium along the vertical profiles of soils of various types, differing in geomorphological position, humidification conditions, and the level of uranium content was analyzed. In general, in the (0–20)-cm layer of undisturbed soils, 46–57% of the uranium inventory in the soil profile is concentrated.

The fractions of uranium associated with the migratory active (located in pore solution), exchangeable, mobile, and fixed forms were determined. It was found that in the soils widely distributed in Belarus, the main amount of uranium (85–96%) was in the fixed form. It was shown that the fractions of ^{238}U in the migratory active, exchangeable, and mobile (conditionally biological available) forms increased from loamy to sandy loam and to sandy soils. The fraction of U_{mob} in mineral and organic soils did not exceed 15%.

The values of K_d coefficient as ratio between activity concentrations of radionuclide in the solid phase and pore solutions of water-saturated soils were estimated. Among the mineral soils, the minimum coefficients K_d (166–282) were characteristic of sandy soils. The maximum coefficients K_d (720–1,400) were found for loamy soils. The relatively high sorption properties of loamy soils to uranium were due to the high (20–40 wt. %) content of the “physical” clay (the particle size of less than 1×10^{-5} m). In organic soils, the K_d coefficient varied over the range of 430–2,780 and significantly depended on the ratio of soluble and hardly soluble organic components and the acidity of the soil.

For some species of soil, the effect of temperature and humidity of the soil on the uranium content in a mobile (conditionally biologically available) form was studied. In general, the genetic type of soil significantly affects the content of U_{mob} in the soil, as well as the degree of change in U_{mob} content as a function of temperature. In air-dry conditions, the maximum U_{mob} content in sod-podzolic light loamy and peaty soils was observed at a temperature of +15 °C. With a subsequent rise in temperature to +30 °C, the content of U_{mob} in both soils was reduced. In water-saturated soils, the maximum U_{mob} content was observed after soil freezing.

For all the temperature regimes studied, the content of U_{mob} in the sod-podzolic medium loamy soil increased with an increase in soil moisture from 5.5 to 60% of the WC. A subsequent increase in soil moisture from 60 to 100% resulted in a decrease in the U_{mob} content, and the levels reached were practically preserved with a subsequent increase in humidity to 140% of the WC. From the data obtained, it follows that freezing the waterlogged soil during the vegetation period can lead to an increase in U_{mob} content, which contributes to the accumulation of uranium by terrestrial ecosystem vegetation.

The information on the uranium species in the soils, as well as on the K_d values can be used for parametrization of models for forecasting the redistribution of uranium in soil media and uranium entering the natural waters and biological communities.

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Environmental and Health Impact Due to Uranium Mining



Rajiv Ranjan Srivastava, Pankaj Pathak, and Mosarrat Perween

Abstract Uranium is a debatable clean source of energy all over the world. The mining of uranium is controversial mainly because of its associated impacts on environment and human health. The conventional way of exploiting the rock-ores either from the surface mining or, heap leaching or, underground mining, aiming the maximum production to fulfil the soaring demand, has posed the significant environmental, economic and social risks. In this context, the technological advancement in mining practices could significantly reduce some impacts compared to the early strategic period, but certainly yet to be considered as the sustainable one. The inevitable water-intensive extraction process is a serious concern along with the handling of mine tailings, which contain thorium, radium, uranium and polonium and emit radon. Therefore, with emphasis on the direct and indirect impacts of uranium mining and associated environmental and health impacts, some cases have also been discussed in the present chapter.

Keywords Uranium · Mining legacy · Environmental hazards · Human health · Mine tailings · Radiotoxic wastes

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1 Introduction

Uranium is a conventional albeit controversial source of energy without emission. The 1 kg of uranium can produce an equivalent energy to 2.2 tons of coal burning. Therefore, most of the developed countries such as the USA, Japan, France and Russia rely on nuclear energy to fulfil their civil and military energy demands (Wang et al. 2018). These two sectors are consuming the most of uranium along with nuclear weapons and limited usage in medical science, agriculture and food processing as preservatives. In order to fulfil the raw material for these uranium-consuming sectors, various countries are involved in mining and processing of uranium ores, mainly as U_3O_8 (as shown in Table 1). A recent report of the World Nuclear Association (2017) reveals that the largest contributing countries are Kazakhstan, Canada and Australia, which share the world's uranium supply of 39, 22 and 10%, respectively.

Being a controversial source of energy, the world is still in dilemma whether to use it or not or how much clean it is in reality (Jin and Kim 2018). On the one side, several countries like Japan, France and South Korea are busy in analysing the benefits of nuclear energy after the Fukushima fallout (Wang et al. 2018). On the other hand, the fastest growing countries like India are eyeing on the potential of nuclear power plants to fulfil the energy demand of the country (IEO 2015; Pathak 2017; Pathak and Sharma 2018). Notably, India has been ranked 12th by producing 421 tons of uranium in the year 2017 but from its low-grade reserves that account 3% of the global deposits (Chaki et al. 2011; World Nuclear Association 2017). To accomplish India's 2030 mission of 21GW nuclear energy, the uranium is being imported from Russia, Kazakhstan, France and Australia (Pathak 2017; World Nuclear Association 2017; Pathak and Sharma 2018). Conclusively, the global demands of uranium do not seem to be lowered down, henceforth, the mining activities will also continue in recent future. Most of the mining activities pose serious threats to the environment and ecological system; uranium is no exception of it. A typical civil nuclear fuel cycle is shown in Fig. 1, which depicts mainly three types of waste generation: (i) tailings (solid residues), (ii) spent fuels (liquid radionuclide waste) and (iii) fission products (solid radionuclide waste). Amongst three types of wastes, tailings are the major in volume after milling and leaching; however, the crushing and grinding also generates the hazardous and radiotoxic fine dusts. Ever since the late 1950s to fuel a nation's nuclear weapons stockpile, most uranium mining (including the milling sites) have been operated and managed under a minimum public health and safety regulation which has recently been implemented (Kikawada et al. 2015). Not only the present activities but also the legacy of large uranium mining and milling waste deposits is a matter of concerns about the exposure risks through the environmental pathways. The unseen and hidden effects can be seen from many studies; some of the foremost concerns are extremely serious, viz. slope stability, land degradation, air pollution, groundwater contamination and bioaccumulation. The fine particles of metal dust mixed with air badly damage the air quality. The wastes generated by the uranium mining, milling, leaching and tailing

Table 1 Uranium mining in different countries

Year	Kazakhstan	Australia	Canada	Niger	Namibia	Russia	Uzbekistan	China	USA	Ukraine	South Africa	India	Czech Republic	Brazil	Pakistan
2007	6637	8611	9476	3153	2879	3413	2320	712	1654	846	539	270	306	299	45
2008	8521	8430	9000	3032	4366	3521	2338	769	1430	800	655	271	263	330	45
2009	14020	7982	10173	3243	4626	3564	2429	750	1453	840	563	290	258	345	50
2010	17803	5900	9783	4198	4496	3562	2400	827	1660	850	583	400	254	148	45
2011	19451	5986	9145	4351	3258	2993	2500	885	1537	890	582	400	229	265	45
2012	21317	6991	8999	4661	4495	2872	2400	1500	1596	960	465	385	228	326	45
2013	22451	6350	9331	4518	4323	3135	2400	1500	1792	922	531	385	215	192	45
2014	23127	5001	9134	4057	3255	2990	2400	1500	1919	926	573	385	193	55	45
2015	23800	5654	13325	4116	2993	3055	2385	1616	1256	1200	393	385	155	40	45
2016	24575	6315	14039	3479	3654	3004	2404	1616	1125	1005	490	385	138	44	45
2017	23391	5882	13116	3449	4224	2917	2404	1885	940	550	308	421	0	0	45

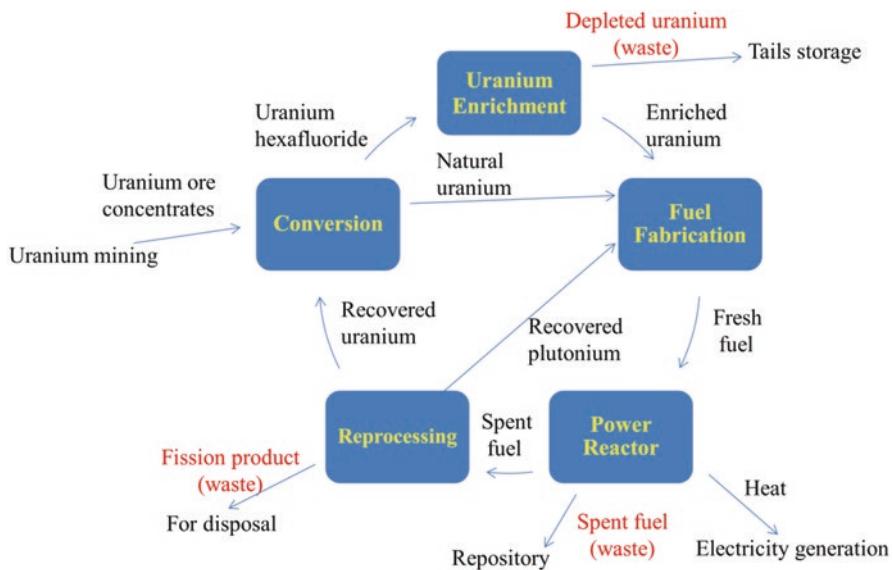


Fig. 1 A fuel cycle in nuclear sector (source: <https://dfat.gov.au/about-us/publications/international-relations/asno-annual-report-2013-14/html/section-2/australias-uranium-production-and-exports.html>)

Table 2 Amount of uranium residues in different activities of mining and processes

Unit of measurement	In situ leaching (ISL)	Underground and open pit	By-product
Tons	29,492	27,350	2689
%	50	46	4

dumps slowly spill to pollute the ground/surface water. Such contamination of the radioactive waste with air and water leads to a gradual decrease in soil fertility (Bajwa et al. 2017), and exposure of it badly affects the human health (e.g. damaging the kidney, liver, lungs, eyes, skin, brain, etc.). However, the societal expectations and safety regulation of the current days evolved considerably as the outcomes of the early mining became apparent to drive the changes in regulatory oversight and mining practices. The reason that is why this industry is directed towards radiation protection, environmental stewardship, health and safety, and the mining methods are changing. In 1990, 55% of the global production of uranium was coming from the underground mines, which shrunk to 33% in 1999. The in situ leach (ISL) mining is steadily increasing its share of the total and in 2017 accounted for approximately half of the uranium production worldwide (see Table 2).

A safer and environmentally low-impact mining is not only a matter of interest to uranium producers, but it is also one of concern to the users of nuclear energy to establish it as the clean source of energy (Ming et al. 2016; Guo and Ren 2017). This chapter aims to be an outline of the leading mining practices and regulatory environ-

ment in which it is being undertaken. The purpose of the chapter is not to blame anyone, but certainly it accounts the leading practices to inform the public debate on uranium mining and to provide the framework approaches to the policymakers to ensure the mining practices in a safe and environmentally responsible manner.

2 Uranium Characteristics, Reserves and Mining Process

Uranium is a naturally occurring silvery-grey element formed naturally in supernova explosions, whereas +VI and +IV oxidation states are most stable in an aqueous medium. The prime contributing natural terrestrial radioactive elements are uranium, thorium and potassium. Moreover, there are different types of minerals, viz. uranite, pitchblende, coffinite, brannerite, davidite, thucholite and thucholite, available in the natural environment (Selvakumar et al. 2018) where ^{238}U (99.27%) and ^{235}U (0.72%) are two natural available isotopes of uranium. Isotopes of uranium are radioactive and fissionable, but only ^{235}U is fissile that support a neutron-mediated chain reaction. Generally, 2–4 $\mu\text{g g}^{-1}$ of uranium found in the earth's crust and more concentrated amount of uranium is present in rock formation which can be mined (Wang et al. 2016). The geological structure of worldwide uranium mine sites is given in Table 3. Usually, there are three ways of uranium ore processing (as shown in Fig. 2), but each one is creating health risks for local resident including the mine workers and causing permanent damage to the environment as mentioned in the following.

2.1 Open-Pit (OP) Mining

The OP mining is used to remove near-surface deposits where the removal of rock and soil is often required to access the uranium ore. This type of mining operation generates ~40 tons of waste for each ton of the processed ore. Also, the seepage from waste rock usually contains uranium in trace amount along with the heavy metals and acids. The rainwater runoffs from OP mines necessitate the development of large evaporation ponds (for storage) and expensive treatment facilities (for processing). The mining activities release dust and emit radon gas, which can end up in waterways causing lung cancer if ingested.

2.2 Underground (UG) Mining

The UG mines are created using several shafts and tunnels in series. Miners must need to go underground for building the machinery and access to the uranium ore. During this activity, the workers get exposed to the high levels of radon. A large quantity of water may proceed to exacerbate release of radon, while the soil subsidence and erosion can affect the neighbouring properties of the geological system.

Table 3 Types and grade of uranium deposits in different countries (after IAEA 2013; Bruneton et al. 2014; Selvakumar et al. 2018)

Types of rocks and minerals	Country	Types of uranium (U_3O_8)
Intrusive deposits: alaskite, granite, pegmatite, monzonites	Canada, Greenland, South Africa, Namibia, South Australia	Low grade
Granite-related deposits: metasedimentary rock granite	Australia, Canada, Czech Republic, Europe	Ordinary and low grade
Volcanic-related deposits: volcanic rocks (uranium associated with molybdenum and fluorite)	Australia, China, Kazakhstan, Mexico, Mongolia, Peru and Russia	High grade
Polymetallic iron-oxide breccia complex: sedimentary rock (uranium associated with copper and iron)	Australia (Olympic Dam is the largest uranium deposit in the world)	High grade
Metamorphite: structurally deformed rocks affected by Na and/or K metasomatism (uranium associated with phosphate)	Australia, Austria, Brazil, Congo, Czech Republic, India, Kazakhstan, Canada	Ordinary and low grade
Proterozoic unconformity: metasedimentary rocks and sandstones	Australia, Canada, India	Low grade
Collapse breccia pipe: coarse fragments and a fine matrix of the penetrated sediments	USA	High grade
Sandstone deposits: sandstone, interbedded basic volcanic ash, ferromagnesian minerals	Australia, Canada, Czech Republic, France, Gabon, Kazakhstan, Russia, USA, Uzbekistan	High, Ordinary and Low grade
Palaeo-quartz-pebble conglomerate: granitic and metamorphic (thorium and rare earths are also present)	Canada, South Africa	Low grade
Surficial: calcite, gypsum, dolomite, ferric oxide and halite, clay, sediments, granite and sandstones	Australia, Namibia	High and ordinary grade
Lignite-coal: silt, clay, sandstone beds	Australia, USA, South Africa, Kazakhstan, Germany	High and ordinary grade
Carbonate deposits: limestone or dolomite	China, India, Kazakhstan	Ordinary and low grade
Phosphate deposits: fine-grained apatite	Central African Republic, Jordan, Morocco, USA	Low grade
Black shale deposits: organic minerals and clays	China, Germany, USA	Low grade

2.3 *In Situ Leach (ISL) Mining*

The ISL mining is a combined technology for mining and extraction process. A mixture of chemical regents or say lixiviant is injected into the earth of mining area via a number of patterned holes. The lixiviant leaches out the uranium along with some impurities from the surrounding rock bodies, and the slurry is collected for the subsequent processing of uranium separation. However, it diminished the surface

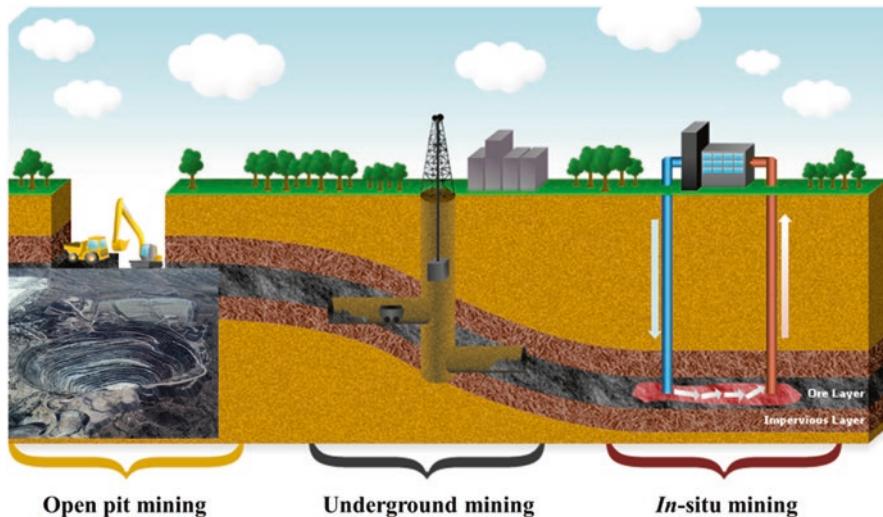


Fig. 2 Typical three types of mining activities mainly used for uranium mining (source: <https://www.hknuclear.com/nuclear/power/cycle/miningandmilling/pages/miningandmilling.aspx>)

and air contamination of the toxic and radioactive dust particulates; the lixiviant once mixed to the underground water can be more serious and would require a long expensive process to restore the aquifer.

2.4 Milling Process

The uranium ore is mined by the OP or UG means of mining; it is subjected to process into a usable form, namely, the ‘yellow cake’. This process is commonly termed as ‘milling’. In which, the ore is crushed and infused with a lixiviant (commonly used sulfuric acid or carbonate solution) that requires large quantities of water. The leach liquor is further undergoing separation and purification steps to recover the uranium in its usable form, and residue goes to tailing as waste to be stored in tailing ponds. Notably, the solid waste residues like rocks, fine sands, etc. coming out from mining activities are known as tailing materials. While the waste rocks are used as a backfill material to fill the voids of excavation, on the other hand, mined water is further reused in ore processing plants after clarification (Sarangi and Kundu 2004). The safe handling and disposal of this waste material are one of the biggest concerns for the researchers, as they contain the radioactive materials that can pose a serious threat of contamination and long-term risks to the geo-environment.

3 Environmental and Health Impacts Due to the Mining Activities

Uranium mining and milling operations have significant environmental, social, and monetary concerns, which have potential to affect quality and quantity of water (surface and groundwater), soils, air and biota (IAEA 2004). Moreover, significant health impacts have been found not only to the miners associated with this activity but also to those who live in the surrounding communities (Bister et al. 2015; Ruedig and Johnson 2015). Significant potential environmental risks are reported with extreme natural and anthropogenic events, i.e. failures in waste management practices. The Chernobyl and Fukushima Daiichi nuclear accidents are examples of anthropogenic accidents (Arnold et al. 2015). Moreover, during the mining process, geological structure of earth is getting disturbed (Beheshti 2011) and leading natural hazards. Therefore, this section analyses the prevailing data on environmental and health impacts from peer-reviewed literature, government and agency reports and various stakeholders to assess the extent of these impacts.

Plenty of the available reports infer that the populations living nearby uranium mining and milling areas may be exposed to higher levels of uranium through the local source of drinking water and locally grown vegetables and food items. For example, a 200-fold mean airborne concentration of uranium has been detected around 2 km area of a Canadian uranium refinery, whereas an elevated level of uranium (and thorium) has been measured around 8 miles from the active uranium mines of Australia. A 75-fold higher uranium concentration has been found in the vegetation near to the milling plants in New Mexico. Although a daily intake of uranium in food and water varies from 1 to $5 \mu\text{g U d}^{-1}$ in the uncontaminated areas, the intake is usually above $13 \mu\text{g U d}^{-1}$ nearer to uranium mining area. The Grant Mineral Belt, New Mexico, was also faced with severe concerns due to seepage of mining and tailing effluents into stream where two tailing ponds contributed ~ 2400 curies of uranium, radium and thorium to the groundwater through seepage. Furthermore, Sethy et al. (2011) have also reported that 1.0 k Bq m^{-3} of radium-contaminated water was found in 43 out of 65 coal mines in Upper Silesian Coal Basin.

Notably, the EPA has measured the most elevated concentrations of uranium in the root vegetation like potatoes and onions and in the animal products (like meat and milk) of the animals taking contaminated grass/plants/foods/vegetation. Earlier studies on health impacts of uranium toxicity show that it may affect the bone growth and have negative reproductive effects. A higher rate of childhood leukaemia, respiratory and kidney disease has also been recorded in the areas proximal to uranium mine sites. Current evidence suggests that the uranium toxicity is primarily due to the chemical damage to the kidney by tubular wall degeneration that can be observed histologically. The damage to the endothelial cells in the glomerulus along with the loss of cellular process and density reduction of the endothelial windows can be observed by the ultrastructural analysis. It leads to a disruption of the tubular solute reabsorption and decreases the filtration rate of the glomerulus, thus causing

the proteinuria. The water-related hazards or legacies from the activities of uranium mining, milling and tailing management potentially damage the kidney. Hence, the containment failure due to the erosion from heavy rain resulting in the release of hazardous or toxic contaminants would be significant for water supplies in the region, leading to 10–20 times greater radioactivity concentrations in the river/reservoir system than what is allowed.

The mining process has a direct impact to the environment (Beheshti 2011), whereas the hydrological cycle is also getting disturbed and contaminated due to the disposal of tailing materials (Dhaoui et al. 2016). Other than the aqueous stream, the solid waste generated by the mining and milling activities contains radiotoxic substances like radon, selenium, uranium and thorium, sometimes along with the heavy metals like molybdenum, copper and arsenic as well. Radon released from the environment poses a risk of lung cancer to both miners and the surrounding population (Meena et al. 2010; Beheshti 2011). Moreover, a significant amount of uranium and thorium was found in plants due to deposition of aerosol emitted from uranium conversion facility area in France. In addition, Vachaspati et al. (2018) have studied aerosol optical properties in the mining zone in Kadapa, India. The elevated level of mining dust increases the mortality rates from non-malignant respiratory diseases, like emphysema. On the other hand, the noise and air pollution by the heavy vehicle used at the mine sites can aggravate the levels of respiratory disease, stress, sleep disruption and blood pressure in the surrounding peoples. In nutshell, it can be stated that mining and milling operations give proximal impacts initially wherein environmental impacts are an intermediate outcome. The final consequences lead to health problems owing to mining and milling activities as summarized in Table 4.

Table 4 Environmental and health impacts during mining and milling operations (after ASTDR 2011; SELC Report 2011; WHO 2012)

Proximal impacts	Environmental issues	Health issues	Permissible limit
Dust and radioactive particulate materials released into atmosphere	Soil, water and air contamination	Diseases like respiratory, lung cancer, kidney and other diseases increase	Soil: 0.1 Bq U g ⁻¹
Waste generated from tailing processes	Accidents due to occupational activities and traffic	Death due to physical injury	Water: 30 µg U L ⁻¹
Transportation issues due to increased truck and heavy vehicles	Noise pollution	Stress, anxiety and mental health issues	Air: Nil
Hazards associated with mining	Decreased recreational activities	increases	Food: 1–5 µg U d ⁻¹
Stigma associated to uranium mining	Local economical sources changes and decreases agricultural and tourism activities	Quality of life such as recreation, community and economic health get disturbed	Human: 0.09–0.23 nCi U 100 cm ⁻²
Occupation			

4 Some Case Study on Uranium Mining Impacts

All over the world, 60% of uranium is mined in Australia, Kazakhstan and Canada, and as per the IAEA report (2013), Kazakhstan is the leading producer of uranium. The IUCN Red Book mentioned in the World Nuclear Association stated that 31% uranium resources are located in Australia, 12% in Kazakhstan and 9% in Canada, whereas 6% and 4% of world's uranium resources are deposited in South Africa and the USA, and only 2% of world uranium resources are found in India. Below few case studies of African countries, Portugal, Canada and India have been discussed.

4.1 Africa

African countries are involved in uranium mining since the nuclear fuel cycle outset. Tanzania, Nigeria, Namibia and South Africa are the major mining countries in Africa. Uranium mined from the Democratic Republic of Congo (DRC) was used in the Manhattan project for the atom bomb dropped on Japan. Uranium mined from South Africa was used to feed the nuclear programme of the USA and UK during the 1960s, while Nigerian uranium was fed to the French nuclear programme. South Africa is the only African country to produce nuclear energy till date; however, Namibia and some other countries also want to establish the nuclear power plant. The legacy of earlier mine waste along with the current mining activities are generating huge amount of hazardous waste. The dust generated during mining and milling operations, thereafter, the tailings generated after the production of yellowcake exhibit low radioactivity; but their mobility gets increased after mined onto the surface. Due to this, the chances of contaminant release and exposure to nuclear radiation get enhanced; hence, uranium mining must be practised under relevant health and radiation protection codes. Many mining activities have witnessed a long environmental pollution and exposure to gamma radiation and radon gas to both workers and public, which can be taken as the negative side of the uranium mining (Fig 2014; OECD 2014).

In contrast, the direct/indirect job creations in the remote area of the African countries can be a potential impact on the society to improve the life of the miner, engineers and labours, more specifically of the local workers. However, this logic gets diminished when looking at the health impacts on the peoples working in uranium mining. The economic benefits can always be measured against the societal gain like human health and environmental pollution. There is a broad impact of uranium mining, but not the financial benefits have a positive effect for the mining country. For example, the revenue generated from uranium exploitation of all the mines in Nigeria has accounted for only 5% of the annual budget (2010) of the country. In the year 2010, the French company AREVA produced 114,346 tons of uranium worth ~4.5 billion \$US, but the Niger government received only the revenue ~460 million \$US (Thiam 2014). On that cost, the negative impact on health

and hygiene of the people and harmful deterioration of the environment cannot be overestimated. In the region of Agadez (nearby uranium mines), there is proven radioactive contamination of water and the environment. Many of the mining area are in the desert with a scarcity of water resources, hence, associated with the availability of clean water, particularly in the city Arlit where the price of 20 L water is sixfolds higher than that of the Niamey (the capital city of Nigeria). On the other side, 270 billion litres of water have been pumped from 1978 to 2004 to run this water-intensive activity (Naino 2014). Each of the Cominak and SOMAÏR mines in Arlit uses $99 \text{ m}^3 \text{ h}^{-1}$ water for treatment of minerals. Consequently, water gets loss from the fossil aquifers along with the problems of water contamination. The 14,000 inhabitants of Arlit can only access water between 3.00 and 4.00 am in the morning time.

In South Africa, the poorly paid workers are often suffering from tuberculosis (TB). For instance, 300 out of every one tenth of a million mine workers alone in South Africa are occupationally exposed to TB. 50% of the migrant women in a mining town near to Johannesburg are found to be infected with HIV (Mtonga 2014). The mining companies, however, are arranging for the health checkup of mine workers, but either it is not regular or unreliable to the workers. The workers of Namibian mines always raise concerns about their health status which was getting worse as a result of exposure to radiation. Workers of Rossing uranium mine ensure that over the years, the situation has improved, but they also have complained that the safety and protective measures were very poor for who started in the 1980s (Shindondola-Mote 2014). Workers do not understand why they have not been informed about the link between exposure to radiation and possible occupational repercussions in their safety manuals. On the basis of submitted report, the IAEA team visited one of the largest and longest running open-pit uranium mine sites of the world and found several cases of TB and lung cancer (IAEA 1992; Kohrs and Kafuka 2014). Therefore, an obvious question is whether the changes came too late for the miners. Moreover, the discrepancy like the Niger who is fueling 80% of French electricity does not have light at home is now causing dissatisfaction amongst the peoples of the country. The Nigerian civil society has alleged to AREVA bringing the irreversible pollution to Arlit by storing above 45 MT mine tailings into the open air. People are having cancerous diseases, the ecological system has lost, and agricultural land is affected by draining 70% of the groundwater layer. The situation due to uranium mining activities can be depicted from Fig. 3.

During the mining operation and more specifically after the closure of a mine, reclamation of the mine site is a prerequisite, which is virtually impossible. Once the rock is dug out, or ore is in situ leached by sulfuric acid, the original state cannot be restored. Only the damage can be controlled up to certain limits. The reclamation cost can be expensive; only a few studies exist by the German Ministry of Economic Affairs (BMWi) and the joint study by the OECD and IAEA. An average reclamation cost has estimated to be $4.0 \text{ US \$ ton}^{-1}$ of tailings if mines extracted only uranium ore; however, the cost reduced to $2.2 \text{ US \$}$ for the mines of gold/copper and uranium as a by-product. For example, Tanzania does not mine uranium as a by-product has high reclamation cost, while South Africa mines recover uranium as



Fig. 3 (a) Miles of empty lands due to the danger of radioactive exposure (source: <https://www.pbs.org/newshour/nation/before-the-u-s-approves-new-uranium-mining-consider-its-toxic-legacy>); (b) the solid rocks and dusts generated by the mining activities in Nigeria by SOMAIR (source: <http://www.mining.com/web/arevas-niger-uranium-mines-cut-staff-slash-production-union/>); (c) the legacy of acid mine drainage after closure of pump station at West Rand basin in South Africa (source: <https://www.iol.co.za/saturday-star/south-africa-not-managing-impact-of-uranium-mining-says-new-report-1101922>)

a by-product of gold costs lower for tailings reclamation. Nevertheless, the joint study by OECD and IAEA asserts high cost to store the uranium mine tailings, which vary between $0.55 \text{ US \$ ton}^{-1}$ to $13.62 \text{ US \$ ton}^{-1}$ of the mined ore. The individual costs of tailing reclamation in a particular country are shown in Fig. 4. As per the ‘polluter pays’ rule, the companies involved in uranium mining should pay for the reclamation costs, but often the reality is found to be quite different. Mining companies either leave the country to dodge such obligations or go bankrupt after the deposits get mined out. Hence, the government and regulatory body need to be strict on this issue to abide the companies to fulfil their societal obligations and to the environment.

4.2 Portugal

The Centre-North of Portugal is the uraniferous region having the most of uranium mines operated as open pits or, underground or, in the combination of both types of mining. The Urgeiriça mine was the largest mill, and chemical treatment plant (1951–2001) in Canas de Senhorim, near the city of Viseu, is now under the decommissioning process (Carvalho 2007). As an estimate, for the total produced amounts of 50–100 g radium and 4370 tons U_3O_8 , the mining activity generates huge amount $\sim 13 \text{ MT}$ of solid wastes, which includes the sands from extracted ores, low radioactivity barren rocks and sludge from the treatment of acid mine drainage. Out of which, $\sim 3 \text{ MT}$ waste is dumped near the facilities of Urgeiriça mine, while others are deposited near the mine sites of Cunha Baixa, Quinta do Bispo and Bica (Carvalho et al. 2005). The dumped wastes are in the forms of low-grade ore heaps (unexploited), mill tailings and sludge. The effluents, surface runoff and mine drainage released into a creek, Ribeira da Pantanha (a tributary to the Mondego River),

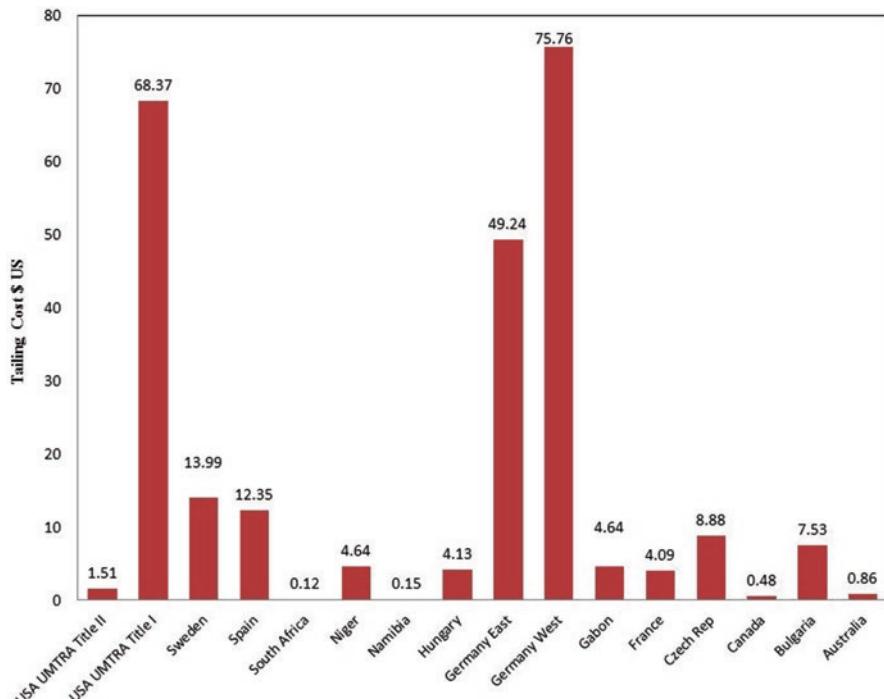


Fig. 4 Tailing reclamation costs in different countries compiled by the German Ministry of Economic Affairs (Wippel 2014)

are causing the dispersal of radiotoxic elements in the environment (Carvalho et al. 2006). Sulfuric acid used for in situ leaching might have infiltrated into groundwater, whereas the contributions from wind erosion and radon emanation enhanced the environmental radioactivity levels, causing the exposure to ionizing radiation above the natural background levels (Neiva et al. 2014).

An assessment of environmental radioactivity, including the Urgeiriça mine, revealed an average ambient radiation of 2.5 mSv a^{-1} at the outside of mining areas in Canas de Senhorim. However, the inside areas affected by the mining activities showed an elevated radiation doses up to 41.2 mSv a^{-1} at the ore discharge area during the milling operation. At the residual dumpsite for extracted ore, the average ambient radiation (18.6 mSv a^{-1} containing elevated concentrations of U-descendants, like ^{230}Th , ^{226}Ra and ^{210}Pb) was higher than that of the sludge dumpsite (3.4 mSv a^{-1}). The acid water of mine drainage from Urgeiriça also displayed a high radionuclide concentration that may runoff to surface water reservoirs and confirmed the role of these transport pathways contaminating the Ribeira da Pantanha by three orders of magnitude (Carvalho et al. 2006; Falcão et al. 2006). The analysis of radio-elements in agriculture soils and water from well used for irrigation purpose has also exhibited

Table 5 Concentration of α -emitting radionuclides detected in different samples

Waste type	Sample description	Radionuclides (Bq kg^{-1})		
		^{238}U	^{226}Ra	^{230}Th
Tailings	Barragem Velha	2530	24717	10337
	Barragem Nova	41598	1690	13390
	Milling station	38316	15569	30115
Acid mine water	Filtered water	2.17	1.48	0.015
	Suspended matter	35.1×10^3	12.1×10^3	1.8×10^3
Runoff water	Surface runoff	13.2	0.672	1.17
	Percolation water	35.7	1.84	1.06

the enhanced concentrations in the vicinity of mining areas. The concentration measured of α -emitters (^{238}U , ^{230}Th , ^{226}Ra) from the mining and milling tailings at the Urgeiriça mine is given in Table 5 (Carvalho et al. 2006). Such a severe exposure causing effects on human health through environmental pathways necessitate the remediation and continuous monitoring of the mining areas (Santiago Baptista 2005), even after the closure of waste disposal sites.

4.3 Canada

In Canada, the uranium ore (pitchblende, UO_2) was discovered in the early 1930s at Great Bear Lake in the Northwest Territories, and exploration began in 1942. Soon after the World War II, uranium exploration gathered pace in 1947, and by 1956, thousands of radioactive occurrences had been discovered. By 1959, 23 mines with 19 treatment plants were in operational condition in 5 districts of Canada (OECD 2014). In early days, the uranium mining was not as safer as it is being operated now, therefore caused several fallouts and left the legacy of large mining and milling waste deposits as the major concerns for a safe environment. The concerns for the damaging caused by the legacy of uranium mining can be understood by the fact that the Port Radium site decommissioned in 1984, but the clean-up and reclamation work was undertaken after a decade, while the environmental monitoring of long-term performance of the abandoned Rayrock Mine site (in 1959) began in 1998. The amount of danger and radioactive hazards left behind the mining can be determined by the facts and figures below.

The Lacnor Mine (1957–1960) produced 2.7 MT of waste; the Nordic Mine (1957–1968) produced 12 MT of waste; the Panel Mine and Mill produced uranium (1958–1961 thereafter 1979–1990) and produced 16 MT of waste; the Pronto Mine (1955–1960) produced 4 MT of waste; the Quirke Mine (1956–1961 thereafter 1968–1990) produced 46 MT of tailings and waste rock; the Spanish-American mill (1958–1959) produced 0.4 MT of waste in Oliver Lake; the Milliken (1958–1964) and Stanleigh (1957–1960) mines and mills produced 20 MT of waste and tailings;

and the Denison Mines Ltd. (1957–1992) produced about 70 MT of waste (OECD 2014). By 1976, the entire Serpent River was badly contaminated with acid and radioactive wastes. Alone in 1978, more than 30 tailing dam failures were reported. Moreover in August 1993, 2 million litres of contaminated water spilled as a power failure from a Rio Algom's Stanleigh mine tailings.

Nevertheless with the passing of time and awareness for human health and the environment, the uranium mining practices have also changed in Canada. The Key Lake operation has set an example evolved over several decades of operation. A sustainable management of water has remained a key issue for uranium mining. Hence, the collection of radionuclide metal-contaminated water is treated within mill effluent treatment system. The source of contaminated water can be used water from reverse osmosis (RO) plant, runoff and seepage water from ore containment or special waste containment areas and the runoff water from the mill terrace. The environmental monitoring infers that the aquatic impacts do not extend beyond the boundary of facilities and are within effect levels predicted. The raffinate obtained after the solvent extraction (SX) operation of the pregnant leach liquor is also treated with lime to adjust the pH and removal of heavy metals as their precipitates. BaCl₂ is used to precipitate Ra-226, while H₂O₂ is used to control the organic contaminants that inadvertently carry over from the SX circuit. All the treated effluents are first stocked in the monitoring ponds, and only after determining the water quality it is released to the environment; otherwise it is sent back for retreatment. Recently added low-pH thickening could significantly control the molybdenum and selenium into the effluent. Notably, the environmental conditions have improved since the open-pit mining operations ended to control the on-site activities of blasting, grinding and transportation that are not needed in present-day milling operation. In the case of tailing management, Canada has better facility as well (Frey et al. 2010). The McClean Lake operation operated by Areva (Canada) is a leading example since 1999, treating the tailings generated by processing of five different ore deposits. Arsenic is the major contaminant therein the tailings in the range of 0.2–20 mg g⁻¹ (Rinas et al. 2010).

The national regulatory body, Canadian Nuclear Safety Commission (CNSC 2010), extensively monitors the environmental effects by the activities of uranium mining, milling and processing facilities, identifies their potential impacts on receiving environment and ensures that licensees are taking all reasonable measures to control the contaminant releases. Effluent and environmental monitoring programmes have been imposed on a risk basis depending on the complexity contaminant released. In addition to regularly reporting the site-specific environmental effects, the Canadian companies involved in uranium mining have instituted a community-based environmental monitoring programme. The programme allows local habitants to assist in identifying the sampling points, sample collections and evaluation of the monitoring data. By the support of the provincial government, the Environmental Quality Committees have been established to improve communication between the industry, government and local habitants. Such activities help to establish the trust in local population that uranium mining does not pose a health or environmental risk.

4.4 India

The Uranium Corporation of India Ltd. (UCIL) working under the Department of Atomic Energy (DAE) Commission has the central responsibility for the uranium mining in India. As per the DAE report (2011), 171,672 tons of uranium (as U_3O_8) is present in ten states of India (namely, Andhra Pradesh, Chhattisgarh, Himachal Pradesh, Jharkhand, Karnataka, Maharashtra, Meghalaya, Rajasthan, Uttar Pradesh, Uttarakhand). These reserves have the capability to produce 0.848 tons uranium for each ton of the processed U_3O_8 , albeit the ore grade is only 0.04–0.06% uranium (NTI 2003). Jaduguda, near Jamshedpur city, located in the state of Bihar (when it started operation in 1967) is the first uranium mine in India. Now it is under the state of Jharkhand and is the deepest mining activity (at 905 m) of India that alone fueling to ~25% nuclear reactors of India (DNA 2014). There are seven uranium mines in Jaduguda and adjacent areas; Narwapahar is the most modern mines in India, while two processing plants are located at Jaduguda and Turamdihi (refer to Fig. 5a,b). As estimated approximately 99.3% mined ore becomes waste during the processing, while the hydrometallurgical sulphuric acid leaching is used to extract 85–95% uranium along with <1% of radium in the leach slurry. Subsequently, the mine effluent water is recycled in the mill processing circuit, but a substantial amount of effluent water still remains unused and released into the environment (see Fig. 5c). However, the effluent is treated for removal of radionuclide and metals in effluent treatment plant (ETP) before releasing to the environment (see the process flow diagram in Fig. 6).

It is well-known fact that the mining and milling operations generate several environmental and health issues have also been encountered by the mine workers and the nearby community of the Jaduguda region. The unsettled particles and toxic substances floating in the air attack to the lungs of local peoples causing asthma (Selvakumar et al. 2018). Although $BaCl_2$ precipitation for the removal of radio-toxic ^{226}Ra from the effluents generated during mining followed by a lime treatment that precipitate the radioactive Th, Po and Pb as the insoluble hydroxides have been



Fig. 5 (a) An outside view of Turamdihi mines (source: <https://ruralindiaonline.org/articles/the-ore-that-breaks-bodies-in-bango>; (b) production of yellowcake after sulphuric acid leach process (source: http://www.spacedaily.com/reports/Indian_Villagers_Oppose_Uranium_Mines_999.html; (c) a 2-mile long pipeline carrying the slurry containing radioactive waste from the processing plant falling into the tailing dam (source: https://www.huffingtonpost.com/entry/india-uranium-mine-jadugoda_us_566b2d2ce4b0fccee16e8dcd)

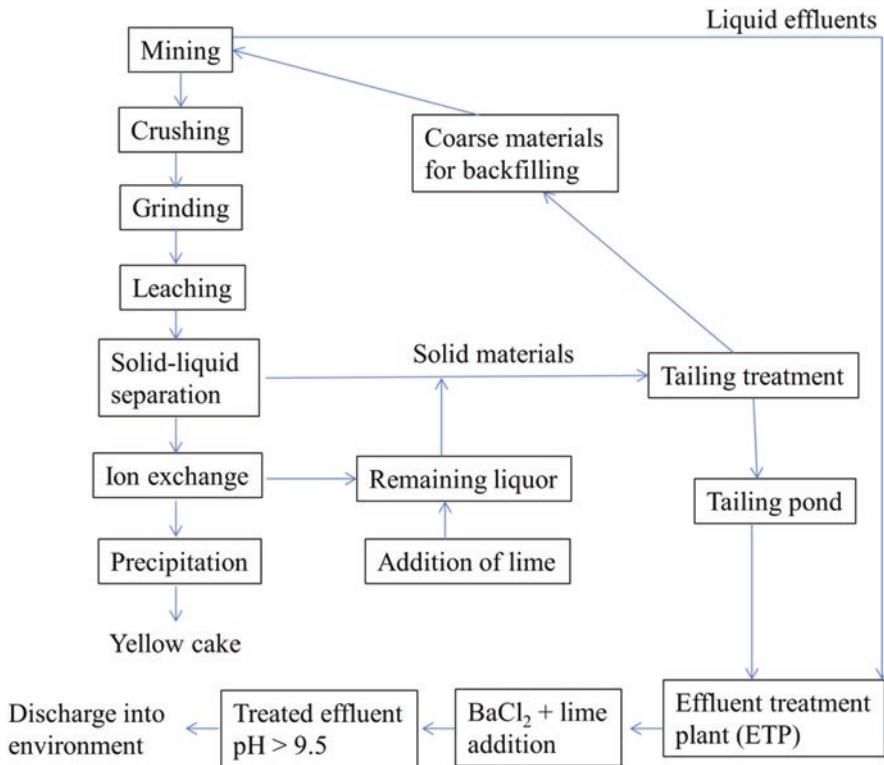


Fig. 6 Uranium ore processing and mine tailing effluent treatment at Jaduguda, India

in practice. The dumping of the radiotoxic metals and heavy metals hydroxide nearby tailing ponds causes a severe impact to the environment. The UCIL and DAE have tried their best to keep the area free from the radiotoxicity; however, the local residents and some NGOs have from time to time raised their voice against the mining activities in the region. The most of the local populations are tribal, and they are often living in doubt for any unusual death (Physorg 2011). In the year 1998, several cases either miscarriages or stillborn babies came in light due to nuclear radiation nearby 5 km radius of a tailing pond (Frontline 1999). Looking at the seriousness of the matter, a committee of the Bhabha Atomic Research Centre (BARC) visited the area in November 1998 at the request of the State Government. The committee examined the whole matter and reported that the concerned cases have no relation to radiation exposure. The genetic abnormalities, chronic malarial infection, malnutrition, head injury sequelae and post encephalitis were the reasons for the death of local tribal people. At that time, the matter was resolved but could not give permanent remedy ever. For instance, in December 2006, due to the pipe carrying radiotoxic waste to tailing ponds was burst and thousands of litres spilled into a nearby tributary to Subarnarekha River for approximately 9 h (Times of India 2015). Several of

such incidents in April 2007, February 2010, and recently in March 2015 have been surfaced, as contaminating the food chain from fish to vegetables and from rice fields to drinking water (Siyemlieh 2018).

The other side of the coin is that the local economy nearby Jaduguda area is mainly dependent on the uranium mines. The local tribal are employed in UCIL and/or involved as daily wage labours, whereas some are involved in the business like transportation and local foods. Due to the government-owned uranium mining, the connectivity to the nearest city Jamshedpur and metro-city Kolkata is easy and very frequent. Of course, the cost of this prosperity is yet to be fully determined, despite the UCIL claiming for a safer mining activity.

5 Recommendations and Conclusions

The world is in the plight for a safer production of uranium mining, by which, the human health and environment are always in a trigger point. The limits for radio-toxic exposure do not allow for a marginal error in the form of mismanagement of waste generated in mining activities or in the form of misoperation. The legacy of the old uranium mining shows bigger problem than the current activities, therefore the stewardship of the mine sites for their remediation is much needed whose cost may vary with the available engineering and technology. The technological advancement should be incorporated in mining and tailing operations to handle and treat the different forms of waste materials in a safer way. Chemical remediation process was found to be costlier, whereas adoption of natural remediation like use of microbial activities can be potent with low maintenance cost. The present mining and milling generated waste must be stored out of the biosphere for preventing the exposure to mankind. The site characterization would be essential for estimating the potential environmental impacts of uranium mining and processing under site-specific conditions and mitigation practices. A regular surveillance is required to ensure that the waste disposal methods do not harm the public health and environment. The weathering of mining waste will continue through decades/centuries; therefore, site maintenance must be foreseen to prevent the removal (intrusion/erosion) of capping materials. Effluent or acid water drainage containing radionuclides may flow to the creeks or water streams (surface/underground); hence a periodic monitoring of environmental radioactivity with corrective measures is much needed. The government/local bodies/regulatory must assure the better environment to live the miners and nearby communities in mining areas, so that they could believe in their reports for the health and environment and utilize the wealth earned from mining activities for their betterment instead of lying on the hospital bed for the treatment of radioactive exposure.

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Biogeochemistry of Uranium in Tropical Environments



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Abstract Uranium evaluation in areas affected by industrial, mining, and agricultural activities is important for the assessment of the human exposure to the natural radioactivity. Besides the occurrence of U isotopes in soils, rocks, and sediments being natural, anthropogenic activities contribute to increase this dose. Food and water ingestion is one of the main sources of U exposure to the population. Although the main U carrier is water, dust and atmospheric particulate matter also act as alternative routes to this radioelement dispersion. In soils, U mobility and its uptake by living organisms can be affected by physical and chemical properties of the mean. Until the present days, most of the studies examining the transference of U from soils, sediments, and natural waters to the biota took place in temperate and developed areas, where the use of the natural resources, climatic conditions, weathering processes, nutrient cycling, and metal uptake by living organisms differ significantly from those in tropical areas. In tropical areas, as soon as organic materials reach the soil surface, they are decomposed, with minimal accumulation of organic matter and a rapid recycling of nutrients and contaminants in vegetation. Mechanisms controlling the uptake of U by aquatic and terrestrial organisms in tropical regions deserve special attention considering that these areas are large producers of food worldwide. In this chapter, we consider the main environmental factors that control the U bioavailability in tropical aquatic and terrestrial ecosystems, providing useful information for risk assessment models.

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1 Introduction

Natural radioelements are part of the chemistry of soils, sediments, waters, and air, resulting in radiological dose for living organisms. Among the natural radionuclides, U, found as three isotopes (^{238}U , ^{235}U and ^{234}U), is the heaviest element naturally present in the Earth's crust. Nevertheless, anthropogenic activities can increase the levels of radioelements in the environment (USEPA 1995; Flues et al. 2006; Fungaro and Izidoro 2006; Papastefanou 2010; Sert et al. 2011; Zhang et al. 2016), as they accelerate the leaching and transporting of the elements through the different ecosystems (USEPA 1995; Flues et al. 2006; Fungaro and Izidoro 2006; Galhardi et al. 2017).

Some of the activities responsible for releasing a great amount of U and other trace elements and radionuclides to the natural environment are related to the mining industry, such as the disposal of waste in tailing piles, the ore exposure to weathering conditions, the generation of acid effluents capable of leaching metals from rocks and soils, and the wet and dry deposition of particulate matter (Berghorn and Hunzeker 2001; Papp et al. 2002; Flues et al. 2006; Mkandawire 2013; Planinsek et al. 2016).

Once emitted in the environment, inhalation, ingestion, and external radiation are the major routes of human exposure to U. Inhalation of insoluble compounds, such as UO_2 and U_3O_8 , can lead to deposition of these compounds into the lungs for long periods, while soluble U compounds, when ingested, can enter into the bloodstream and eventually reach the kidneys or other internal organs (Veiga et al. 1998). About 70% of the U absorbed by blood is filtered by the kidneys and excreted in the urine (Mkandawire 2013). One of the main sources of exposure to U and its decay products related to occupational exposure is underground mining. Veiga et al. (2004) found, in the underground mine in Southern Brazil, occupational exposure due to radon decay products about 30 times higher than the world average dose.

Although it is known that anthropogenic activities can lead to the increment of U concentrations in the ecosystems and consequently the contamination of the aquatic and terrestrial environments, only a few investigations about the exposure of this element to the biota were performed in tropical zones (Garty et al. 2003).

In tropical areas, the climatic characteristics, environmental and weathering processes, nutrient recycling, and the radionuclide uptake or absorption by living organisms differ significantly from the temperate zones (IAEA 2010). According to Carreras et al. (2009), it is essential to hold studies in cities from developing countries and in tropical areas where the sociodemographic-economic characteristics of local population differ considerably from those in developed and temperate countries. Thereby, this chapter summarizes the knowledge about U biogeochemistry in tropical environments, focusing on Brazilian fields and aiming to bring some specific characteristics of the geochemistry of U in tropical areas and related risks to aquatic and terrestrial organisms.

2 Geochemistry of U in Natural Waters and Sediments

Minas Gerais State in Brazil had been an important gold mining center for Portuguese people in eighteenth century. However, the radioactivity observed in their lands in the early twentieth century coupled to its use for the energy generation brought a new scenario to the state that plunged into the “nuclear era” and served to the development of several geochemical studies focusing the presence of U in natural waters and sediments. The interest for radioactive elements there started in 1929 with the pioneering studies held by Djalma Guimarães in Brazilian Geological and Mineralogical Service (SGMB), who proposed a new method for the separation of a high-grade pure U for use in geochronological determinations. In 1935, Ouro Preto, also in Minas Gerais State, was the birthplace of a complete laboratory for mineral analysis that began in 1941 a systematic analytical study of minerals and radioactive waters of that state. Djalma Guimarães in 1948 observed the radioactivity in some rocks of the alkaline suite of the Poços de Caldas plateau, as well as in Minas Gerais State, which was associated with zirconium ore, thus, awaking new interest in more specific investigations at that region.

Morro do Ferro consists of a hill situated near the center of the Poços de Caldas plateau that initially drew the attention of mining prospectors due to the abundant occurrence of magnetite veins and dikes. In 1935, the Minas General Company obtained concession for the extraction of iron and associated minerals at Morro do Ferro area. In the 1950s and early 1960s, preliminary ground investigations of the Morro do Ferro area were carried out by the National Research Council (CNPq), National Commission of Nuclear Energy (CNEN), and National Department of Mineral Production (DNPM) in collaboration with the US Geological Survey (USGS). In 1953, these investigations revealed by aerial radiometric surveys a strong radioactive anomaly of the deposit that is almost entirely due to thorium and its daughter products, associated with rare-earth elements and minor uranium (Tolbert 1955; Wedow 1967). These early investigations included ground surveys, drilling, trenching, gallery construction, geochemical analysis, and mineralogical studies, with a view to evaluating the potential of the ore body. In 1970, it was discovered the Osamu Utsumi Mine in Cercado field at Caldas municipality, distant about 25 km south of the Poços de Caldas city. Such mine was the first in Brazil that produced “yellow cake” (uranium concentrate), originating the Poços de Caldas Mineral-Industrial Complex (CIPC) that belonged to Brazilian Nuclear Industry (INB).

New interest in Morro do Ferro area arose in the 1970s with the suggestion that the deposit could be used as a natural biosphere analogue for a radioactive waste repository as the activity in soils of the area was so high that the natural foliage could easily be autoradiographed. The Biophysics Institute (Federal University of Rio de Janeiro (UFRJ)) and the Institute of Environmental Medicine (New York Medical Center), in collaboration with the Pontifical Catholic University (PUC) of Rio de Janeiro and CNEN, realized several studies focusing the radionuclide mobility.

The Swedish Nuclear Fuel (SKB) and Waste Management Co. managed an international project entitled “Poços de Caldas Project” with the participation of Brazil (INB), Sweden (SKB), Switzerland (NAGRA), the United Kingdom (UK DECC), and the USA (US DOE) (Chapman et al. 1992). The Osamu Utsumi open-pit uranium mine and the Morro do Ferro ore deposit were selected for natural analogue studies, i.e., they were considered natural systems in which the chemical and physical processes were studied as the conditions were expected to occur in the vicinity of radioactive waste repositories. The main key objectives of the project consisted of (1) checking of equilibrium thermodynamic codes and databases, (2) determining the mobility of colloids and their role in the radionuclides transport, (3) modeling the geochemical evolution of redox fronts, and (4) evaluating the migration of rare-earth elements and uranium/thorium series radionuclides during periods of hydrothermal activity (Chapman et al. 1992).

Figure 1 shows the location of the Osamu Utsumi and Morro do Ferro sites. Figure 2 illustrates a typical alpha spectrum obtained for uranium extracted from one groundwater sample collected at Morro do Ferro, in which are evident the peaks of the natural U isotopes ^{238}U and ^{234}U and ^{232}U spike added for checking the chemical yield and providing the U concentration value. Figure 3 shows the results obtained for the dissolved U content in groundwater from bores drilled at Morro do Ferro that were sampled in May 1983 and September 1983, as well as the rainfall in the same period. May 1983 was a period of very low rainfall, and the dissolved U contents were the lowest in all bores, except in SR-9. September 1983 was the beginning of the rainy period immediately after the typical droughts affecting the months of July and August. The dissolved U contents increased in all bores during September 1983, except in SR-4. Thicker clayey packages implied on lower amounts of U leached by infiltrating waters as indicated the inverse significant relationship between these parameters for the waters sampled during the beginning of the wet season (September 1983) (Fig. 4).

Several campaigns for sampling waters and fine sediments (particulate matter) of South Stream at Morro do Ferro area were carried out by Grimaldi (1981) using a manual sampler. The U concentration and $^{234}\text{U}/^{238}\text{U}$ activity ratio data as reported in Table 1 allowed the application of the U isotopes method developed by Moreira-Nordemann (1980, 1984) in order to determine the weathering rate in the region. The database for rock, water, and sediment samples permitted the estimation of a solubility coefficient for U corresponding to $k = 0.44$ in the area, which implied that 44% of the available U in rocks is taken into solution during the weathering process (Bonotto et al. 2007). Using all available data and applying the equations established by the U isotopes model, Bonotto et al. (2007) estimated a value of 0.015 mm yr^{-1} for the weathering rate v at the Morro do Ferro region and concluded that one vertical meter of rock needs about 67,000 years to be weathered, demonstrating thus the chemical weathering rate of rocks under tropical climatic conditions.

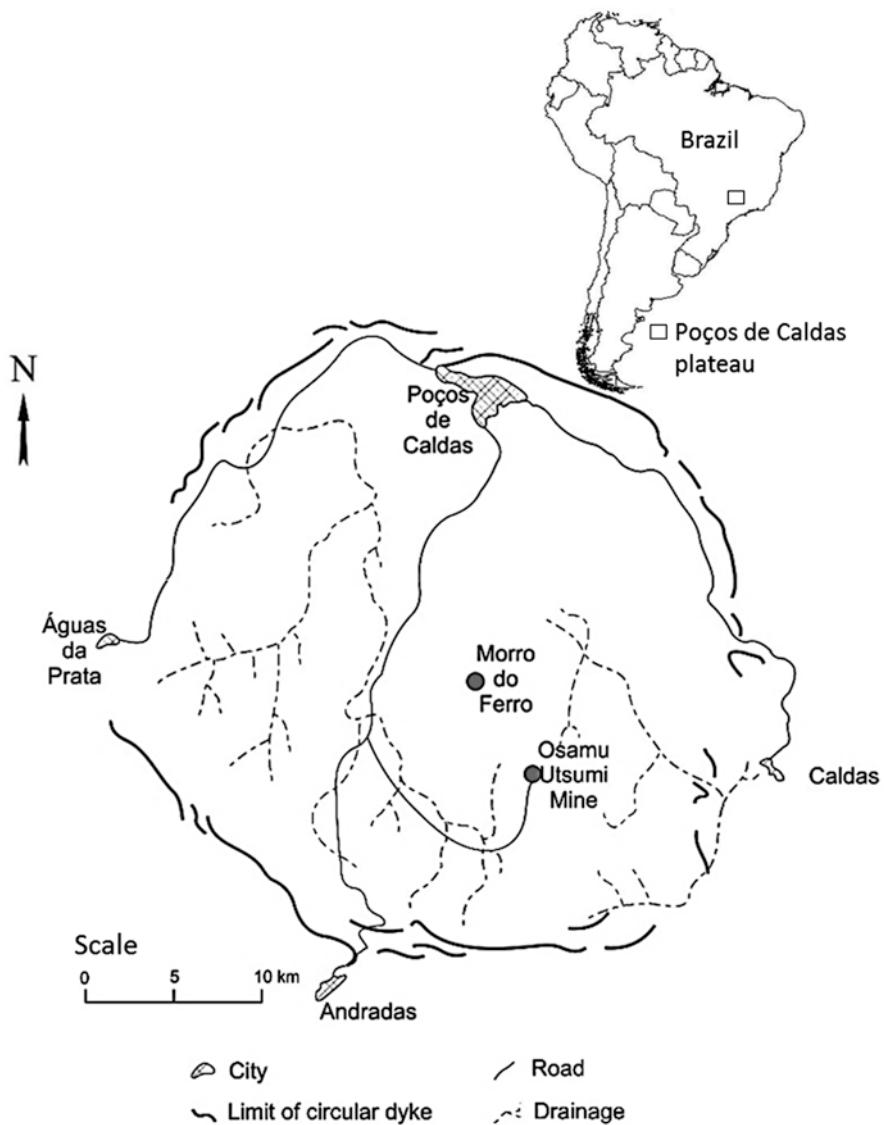


Fig. 1 Location of two important radioactive deposits at the Poços de Caldas alkaline massif, Minas Gerais State, Brazil. Modified from Holmes et al. (1992)

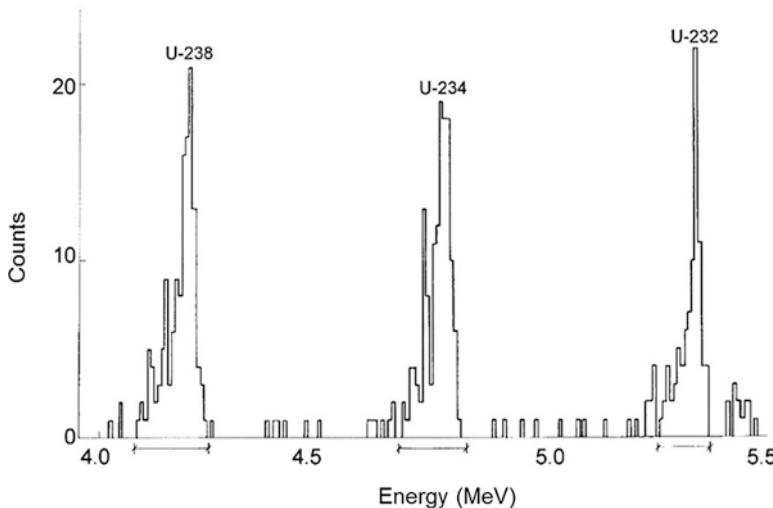


Fig. 2 The alpha spectrum obtained for uranium extracted from one groundwater sample collected at Morro do Ferro, Poços de Caldas plateau, Brazil. Volume = 19.4 L. Counting time = 5.17 h. U concentration = $0.72 \mu\text{g L}^{-1}$

2.1 Toxicity and Uptake of U by Aquatic Organisms

Uranium is a naturally occurring element in the environment and normally is found at very low concentrations in natural aquatic systems. Nevertheless, U exposure can induce harmful effects in the living aquatic organisms including cytotoxic, genotoxic, and teratogenic effects (Lourenço et al. 2017). The U contamination is capable to affect the aquatic organisms at the biochemical, cellular, individual, population, and community level (Franklin et al. 2000). Knowledge about environmental and bioavailable levels of U is important to the maintenance of the environmental health of aquatic ecosystems.

U occurs in natural surface waters at three oxidation states (U^{4+} , UO^{2+} , and UO_2^{2+}), depending on the physicochemical parameters of the environment (Markich 2002). The uranyl ion UO_2^{2+} is the most stable U species in oxic conditions and the most prevalent U species in the environment (Sheppard et al. 2005). Factors such as pH, Eh, presence of chelating agents, concentration and type of organic and inorganic ligands, mixing rate and movement of the water, and reactions of adsorption, desorption, complexation, and precipitation directly influence the U behavior and consequently its speciation (Galhardi et al. 2017). In solutions, adsorption is an important mechanism that controls U activity concentration (Prikryl et al. 2001).

The U presence in natural environments can induce biological effects via its radiological and chemical pathway, representing a unique challenge for bioavailability and toxicity studies (Barillet et al. 2011). Although the radiological impact

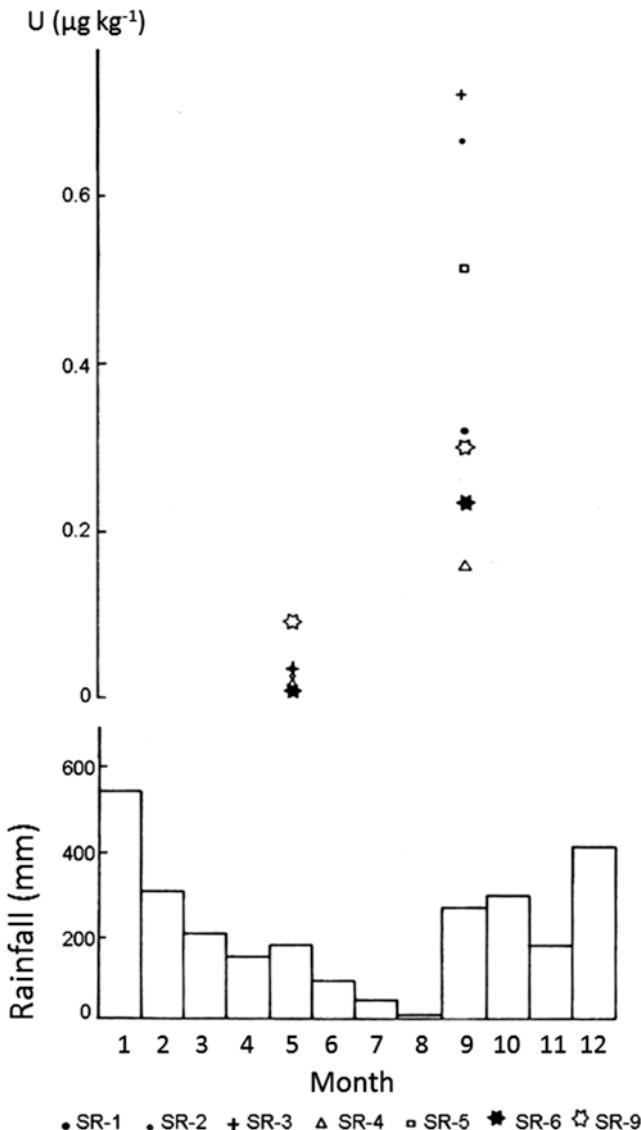


Fig. 3 The dissolved uranium content in groundwater from Morro do Ferro area, as well as the monthly rainfall during 1983

of U is important and might not be neglected, the U toxicity and bioavailability to aquatic organisms is mainly associated with the chemical properties. The U bioavailability and toxicity is strongly influenced by environmental conditions as well as its speciation and geochemistry.

Fig. 4 The dissolved uranium content in groundwater from Morro do Ferro area collected in September 1983 plotted against the total clay layer thickness

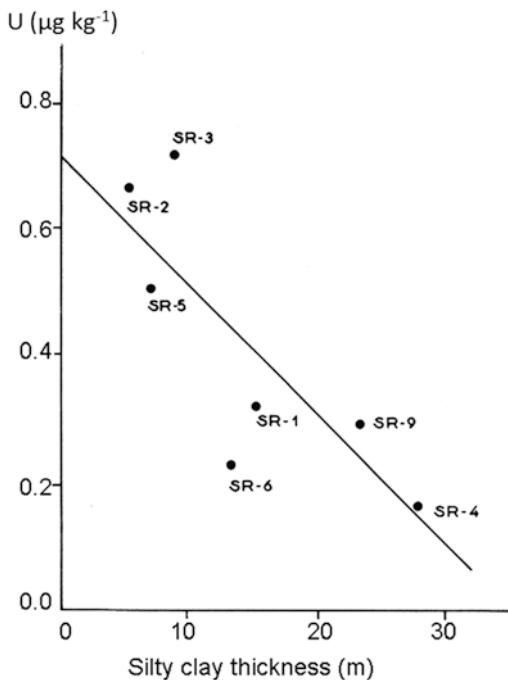


Table 1 Uranium concentration in surface waters at Morro do Ferro and vicinity sampled from June 1980 through July 1981

Parameter	Unit	Site	Number of samples	Average value
^{238}U in filtrate	$\mu\text{g L}^{-1}$	All locations	67	0.23 ± 0.12
		South Stream	43	0.32 ± 0.18
^{238}U on filter	$\mu\text{g L}^{-1}$	All locations	68	0.10 ± 0.01
		South Stream	39	0.10 ± 0.02
$^{234}\text{U}/^{238}\text{U}$ in filtrate	—	All locations	67	1.33 ± 0.04
		South Stream	43	1.26 ± 0.05
$^{234}\text{U}/^{238}\text{U}$ on filter	—	All locations	68	1.07 ± 0.03
		South Stream	39	1.07 ± 0.03

All analytical uncertainties correspond to 1σ standard deviation. According to Grimaldi (1981)

A variety of physicochemical parameters of the water chemistry influence the U toxicity and bioavailability for aquatic organisms (Jha et al. 2016). These parameters can influence the toxicity of U by decreasing or increasing the concentration required to generate a biological response (Chapman 2008). It has been related a decrease in the toxicity caused by waterborne U in response to water hardness (caused possibly by the competition between the U and the Ca and/or Mg for the membrane ligands) (Riethmüller et al. 2001; Charles et al. 2002). The increase of pH was also demonstrated to decrease the biological effects caused by the U

(Markich et al. 2000). The complexation with the DOM (Hogan et al. 2005), carbonate (Nakajima et al. 1979), and phosphate (Fortin et al. 2002) was also demonstrated to decrease the U toxicity due a reduction on the UO_2^{2+} activity.

The UO_2^{2+} and UO_2OH^+ are considered the most bioavailable U species and represent the major threat for aquatic organisms (Markich et al. 2000). However, in some situations, other U species (e.g., $\text{UO}_2(\text{CO}_3)_2^{2-}$) might represent the bioavailable fraction of U (Croteau et al. 2016). A diversity of studies using analytical biological approaches including toxicity tests, bioaccumulation evaluation, chemical speciation techniques, and computational methods were already performed to understand the mechanisms involved on the bioavailability of the U species and/or their toxicity to aquatic organisms.

Due to the heterogeneity of natural aquatic systems, the presence of diverse compounds, and the complexity of biological systems, the representation of the whole mechanism involved in the bioavailability and toxicity of U in the environment is a challenging task for any technique (Eismann et al. 2018). Furthermore, each organism has different uptake mechanisms, internalizing different fractions of contaminants. In this sense, it is observed the organism-specific concept of the bioavailability. The understanding of each mechanism which is occurring in each exposure scenario is important. Integrative strategies employing more than one approach are a powerful tool to improve the understanding about bioavailability and toxicity trends of the U in natural aquatic ecosystems (Ferrari et al. 2017).

Analytical methods are useful to determine different fractions/species of U potentially bioavailable to aquatic organisms. However, no single method can provide unequivocal information about the U behavior in the natural ecosystem (Markich 2002). Physical separation techniques are employed to separate the U species based on size (e.g., ultrafiltration (Guo et al. 2007) and size exclusion chromatography (Trenfield et al. 2011)). Physical separation techniques are also employed to separate U species based on charge (e.g., electrophoresis (Pacheco and Havel 2001)).

Electrochemical methods and the diffusive gradients in thin films technique (DGT) (Drozdak et al. 2016) are also employed to determine labile (weakly complexed) U species. Computational methods rely on the inputted information of the researcher and use mathematical equations to generate a profile about the chemical speciation of a given medium based on a speciation model. While there are several limitations to their use, they provide useful information when applied properly. Also, computational methods represent an advantageous tool to be used complementarily with field experiments performed in the natural systems (Markich 2002).

When studies are performed using biological responses or bioaccumulation, biological factors such as feeding habits, depuration, and movement on the environment should be considered to interpret and compare the data obtained through the chemical and biological approaches (Eismann et al. 2018).

Previous studies have indicated that the U uptake by aquatic organisms is directly related to the concentration of the bioavailable species in the water, suggesting the direct exposure to the water as a main source of U (Bunn 2007). For some U species, the food ingestion represents the main source of this element (Bergmann et al.

2018). Interspecific differences in the sensitivity to U, mainly caused by differences on their trophic status, were observed between freshwater fish (Bywater et al. 1991) species exposed to the same source of contamination.

The U present in natural waters can be bioaccumulated by aquatic biota (Fig. 4) and is sometimes biomagnified through the food chain, representing a potential hazard to the organism itself and to other organisms, which can include human beings (Bergmann et al. 2018). The bioaccumulation process relies on the differences between the assimilation and depuration capacities of a given organism (Pauget et al. 2017). Many studies have demonstrated the ability of aquatic plants to accumulate U in concentrations higher than the water they are exposed to (Favas et al. 2014, 2016). The high bioaccumulation capacity of some aquatic plant species supports its potential use in phytofiltration of waters contaminated by U (Cordeiro et al. 2016). Uranium accumulation was also observed in the periphyton community, with no evidence of negative impact on the productivity and biomass (Bunn 2007). In general, U accumulation is observed in the aquatic biota, inducing effects of different levels in the biological communities (Simon et al. 2018).

The ecotoxicological data about U is abundant for many aquatic species, which is widely used to establish water quality guidelines (Sheppard et al. 2005). Ecotoxicological tests using local freshwater organisms are performed since the 1980s (Cheng et al. 2010). Classical endpoints of ecological relevance in terms of population dynamics include mortality, growth, reproduction, and morbidity (Beaugelin-Seiller et al. 2012). Extensive information about early and sublethal effects of the exposure of aquatic organisms to high U concentrations is available. Measurements of neurotoxicity (Barillet et al. 2007), oxidative stress (Reis et al. 2018), and genotoxicity (Barillet et al. 2011) were used as endpoints to understand the primary subcellular damage caused by U interaction with the biota. Increased physiological effects were also observed across generations of microcrustaceans exposed to U (Massarin et al. 2010). However, knowledge about the trends of the U interaction with aquatic organisms under environmentally realistic concentrations found in natural waters is still not well-established, mainly in tropical regions.

A few examples of bioaccumulation and toxicity tests can be found in the literature focusing on tropical freshwater and aquatic organisms. For example, Ferrari et al. (2017) investigated the U toxicity of aquatic organisms in the vicinity of the Osamu Utsumi mine, at Poços de Caldas city, Brazil. Chemical analysis and acute toxicity tests using two species of microcrustaceans (*Ceriodaphnia silvestrii* and *Daphnia magna*) were conducted in threatened U mine effluents and waters of the Antas Reservoir. The spatial distribution of the U concentrations was similar to the acute toxicity observed for both species. Furthermore, the data obtained demonstrated that the variation in water hardness (mainly related to the treatment of the effluents) considerably influenced the toxicity to microcrustaceans. Water hardness was demonstrated to have a protective effect to the aquatic species studied. This study provided very useful information about the U toxicity to aquatic organisms in tropical areas, since *C. silvestrii* is a microcrustacean species widely distributed throughout South America.

Considerable amount of information about guideline values for the protection of the environment concerning the U contamination exists. However, the values obtained for a given species in each area might not be extrapolated for the wide variety of conditions observed in the whole natural aquatic ecosystems. Since many environmental conditions might influence the U speciation and consequently its bioavailability and toxicity, every generalization including a wide number of species might be taken very carefully, and more investigations for the tropical conditions must be performed.

3 Geochemistry of U in Tropical Soils

Tropical regions are located between the Tropics of Cancer and Capricorn and are characterized by high annual temperature and rainfall, which results in high weathered soils. The warm humid climates cause soil acidification and can affect the U distribution in soils. Besides tropical soils being considered vulnerable to radioactive contamination (Wasserman et al. 2008), studies related to the geochemistry of U in tropical areas are still scarce (Kritsananuwat et al. 2015; Ribeiro et al. 2018) mainly due to the complexity of the soils (Wasserman et al. 2008).

Overall, the mineralogy of U is well documented in the literature (e.g., Romberger 1984; Bernard 2003; Kabata-Pendias 2011). Uranium can be found in all rock types, commonly in small concentrations. The average U concentration in the Earth's crust is 2.7 mg kg^{-1} (Taylor 1996). The mean concentration of U in rocks decreases in the following order: granitic rock (3 mg kg^{-1}) > basic rock (1 mg kg^{-1}) > ultrabasic rock (0.001 mg kg^{-1}). Uranium content in sedimentary rocks varies according to the redox conditions during their formation (Turekian and Wedepohl 1961). Compared to the mantle, U is concentrated in the Earth's crust, and its content ranges from 0.013 mg kg^{-1} for the undepleted mantle (Bjorlykke 1974) to 0.032 mg kg^{-1} for the present mantle (Burt and Sheridan 1980).

Uranium is present in the pedosphere as a result of three main pathways: as part of the Earth's layer (primordial radionuclides), originated from the cosmic ray interactions, and as a consequence of anthropogenic sources (USEPA 2006). The average concentration of U in soil ranges from 0.79 to 11 mg kg^{-1} (Kabata-Pendias 2011). Total U content in soils depends on the composition of the underlying bedrock and the intensity of the weathering, which can sometimes result in a higher content of U in the geologic material. For example, Cunha et al. (2018) investigated the geochemistry of U in soils from the largest uranium-phosphate deposit in Brazil and observed concentrations higher than 900 mg kg^{-1} .

Nevertheless, U concentrations in soils are not only influenced by their parent material but also by abiotic and biological processes (Ribeiro et al. 2018). Consequently, the geochemistry of U in soils and the human external exposures to radiation is not homogeneous, varying according to the geological context, climatic conditions, and other environmental characteristics (UNSCEAR 2000). The main anthropogenic sources of U in the soils are the fuel fabrication, fuel reprocessing, U

mining and milling, U processing, phosphate, coal and metallic mining, and inappropriate waste disposal (Gavrilescu et al. 2009).

The geochemistry of U in tropical soils depends on soil types and their properties (Ribeiro et al. 2018). Several factors influence the solubility of U in tropical soils, such as pH, oxidation-reduction potential, concentration of complexing anions, soil porosity, particle size distribution, organic matter content, sorption properties, and others. Uranium retention in soils can occur by adsorption, chemisorption, ion exchange, or a combination of several mechanisms (Allard et al. 1982; Vandenhove et al. 2007).

Uranium is characterized as a lithophile element and can exist in the trivalent (U^{+3}), tetravalent (U^{+4}), pentavalent (U^{+5}), and hexavalent (U^{+6}) states. The U^{+4} and U^{+6} states are the most important in mineralogy (Romberger 1984). Uranium is a reactive metal, and, as a result, it combines with other elements in the soil to form U compounds. In soils, U is usually found in the oxidized form. Abiotic and biological processes are responsible for chemical reactions that alter the oxidation states of U (Yamaguchi et al. 2009). Because most of the tropical soils exhibit pH between 4.0 and 7.5, the hydrolyzed form of U (U^{+6}) predominates in soils. Under acid ($\text{pH} < 5$) and oxidizing conditions, typical characteristics of tropical soils, U exists predominantly as uranyl (UO_2^{2+}). Under conditions close to neutrality, the common U forms are soluble complexes, such as UO_2OH^+ , $(\text{UO}_2)_2(\text{OH}_2)^{2+}$ e $\text{UO}_2(\text{HPO}_4)_2^{2-}$. At higher pH, several carbonated complexes predominate (i.e., $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$) (Langmuir 1978; Gavrilescu et al. 2009).

Mineral colloids and organic complexes also influence the geochemistry of U in soils (Chen et al. 2018; Santos-Francés et al. 2018). Studies have shown that both clay minerals and humic acids can affect the solubility and mobility of U in soils (Bednar et al. 2007; Mibus et al. 2007; Wang et al. 2014), depending on the mobility of the humic acids and mineral colloids and their capacity to retain U. For example, uranyl has a high affinity to be complexed with fulvic and humic acids (Kim 1986). Some of the minerals acting as important sorbents of U in soils are feldspars, kaolinite, goethite, and montmorillonite (Catalano and Brown 2005; Kabata-Pendias 2011). The adsorption of uranyl by clay minerals as well as by oxides and organic matter is an important process controlling the geochemistry of U in solutions, since it might reduce U anomalies in surface waters (Rose 1994). In solid phase, the physicochemical characteristics of the soils and sediments control the bioavailable fraction of U (Galhardi et al. 2017); thus, understanding U geochemistry is an important tool to predict the risks of this element to terrestrial organisms.

3.1 Bioavailability of U in Soils and Soil-to-Plant Transfer Mechanisms

The fate of U in the natural environment is of great importance. Worldwide, the contaminant bioavailability has been considered for the assessment and remediation of contaminated soils. There is an increasing concern about the significant persistency of metals and radionuclides in soils and their potentially high

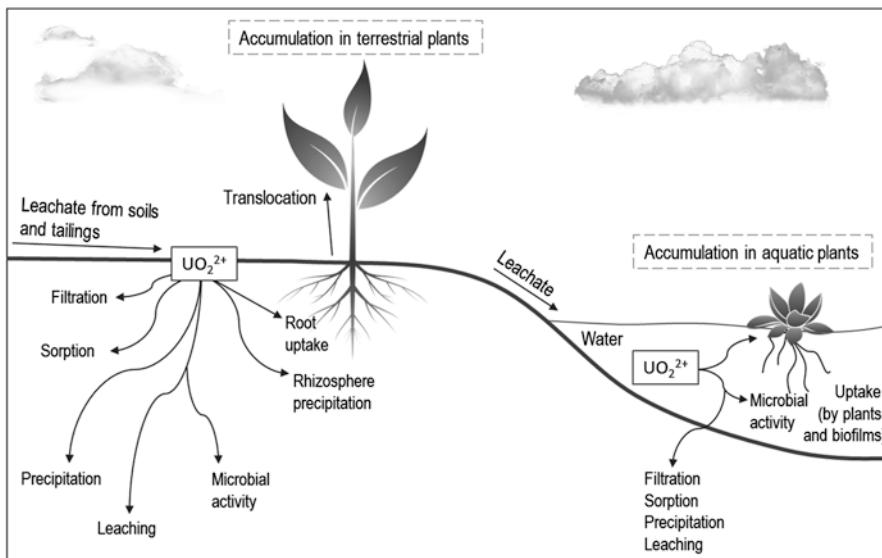


Fig. 5 Principal mechanisms of uranium mobilization in the soil-plant and water-plant systems. Modified from Fava et al. (2016)

health risks due to the long-term consumption of contaminated crops (Abraham et al. 2018).

Figure 5 illustrates the main routes of U in the plant-soil and plant-water systems after this element is leached from soils, tailings, and rocks. Uranium can be assimilated by the roots of terrestrial plants and translocated to the shoots. There is an increasing concern about the significant persistency of U in soils and its potentially high health risks due to the long-term consumption of contaminated crops. Accumulation by aquatic plants is also possible, after U is transported to the natural water systems, representing a hazard for both terrestrial and aquatic ecosystems. Thus, in order to estimate effects and potential risks associated with elevated U concentrations that result from natural weathering of mineral deposits or from industrial, mining, or agricultural activities, the fraction of this element in the soils that are bioavailable must be identified, since the accumulation of elements from soil to plants has been found to be better correlated with their bioavailable concentrations (Alvarenga et al. 2014) when compared to the total content in the soils.

Chemical extractions have been widely used to evaluate the available portion of metals in agricultural soils, as well as recently developed methods to measure the free metal ion activity in the soil pore water, such as DGT, WHAM/Model VI, and NICA-Donnan model (Markich et al. 2000; Kim et al. 2015; Drozdak et al. 2016).

Nevertheless, biomonitoring tests are usually preferred over traditional chemical assays of the bioavailable portion of radionuclides in soils, mostly because bioassays give a more direct measurement of biological responses without the need of significant interpolations (Kim et al. 2015). Besides the advantages provided by the biomonitoring when compared to the traditional chemical extraction methods, some

disadvantages are associated with the use of bioassays, since they are often time-consuming, laborious, and with a high cost (Kim et al. 2015).

Predicting soil-to-plant transfer is another important step to assess U bioavailability in terrestrial ecosystems. One of the main sources of U exposure to the population is through the food ingestion. The most common index used to estimate the radionuclide transport and their accumulation in vegetables is the transfer factor (TF), defined as the ratio between the concentration of the element in plants and in the soil. The TF describes the amount of the element that can be absorbed by a plant from its substrate under equilibrium conditions, assuming that the accumulation is directly proportional to the concentration of the element in the soil (Sheppard and Sheppard 1985).

Soil parameters that might affect the U concentration in the mean, its mobility in the rhizosphere, and its availability to plants are the soil pH, electrical conductivity, cation exchange capacity, total organic carbon, nutrients, mineralogy, and climate, in addition to (bio)chemical processes such as complexation, precipitation, cation exchange, and redox reactions (Ehlken and Kirchner 2002; Shtangeeva 2010; Sohlenius et al. 2013; Gupta et al. 2014; Zhao et al. 2016).

Overall, processes controlling U activity in soils are dependent of chemical and physicochemical characteristics of the geologic material exposed to weathering conditions (Arbuzov et al. 2012). Uranium present in the mining residues may be complexed by chelating agents produced by microbial activity mainly under reducing conditions, favoring its mobilization and consequently its bioavailability to the biota (Francis 1990).

Although the uptake of metals by plants can be affected by numerous biogeochemical factors, in about 50% of the investigations focusing on the TF, they were not considered (Vandenhove et al. 2009), which limits our understanding on the U uptake by plants, mainly in tropical regions, where the chemical and bioassay methods were less applied to investigate U uptake by terrestrial organisms.

An assessment of the U distribution in the soil-plant system may be also rather complicated because there is little information related to the rate of U uptake and storage by different plant species and different parts of the plants (Shtangeeva 2010). Effects of the soil properties and natural differences in the ability of plants to assimilate U may be some of the reasons why concentrations of this element differ significantly in various plant species (Galhardi et al. 2017).

Availability of U contributes to the degree of its transfer to plants, but other factors could help in understanding potential risks related to levels of radioactive elements in soils, from molecular to individual and ecological scales. In general, the biological factors are less well understood than the geological factors controlling the U availability in soils (Willey 2014). Only complex models considering soil and biotic characteristics could help in predicting U uptake by terrestrial plants, as TF is not related to simple bioavailability parameters (Vandenhove et al. 2009).

Besides some researchers investigated the absorption of radionuclides by species of plants in tropical areas (e.g., Vasconcellos et al. 1987; Santos et al. 1993; Lauria et al. 1994; Santos et al. 2002; Mazzilli et al. 2012); a systematic investigation focusing on areas affected by industrial, agricultural, and mining areas was not

performed, even though it's well known that the cultivation of organic soils is an important human exposure pathway of trace elements and radionuclides (Saetre et al. 2013). It's essential and necessary thus to understand the differences on the accumulation of U by the different plants, especially considering the edible portions of the vegetables, since data on the element concentrations might be very useful for radiological risk assessments (Staven et al. 2003) and for predicting the fate of the contaminants in the environment and in the food chain (Willey 2014). Thus, mechanisms controlling the TF of U in tropical regions are of a great concern, considering that these areas are large producers of food worldwide (Fig. 5).

4 Conclusions

The evaluation of radionuclides in tropical areas is important for the assessment of human exposure to the natural radioactivity, especially in those areas affected by agricultural, industrial, or mining activities. Geochemical and environmental factors may affect U availability for both aquatic and terrestrial organisms (discussed in previous sections).

In the aquatic environment, the risk of the presence of bioavailable forms of U is well known. Uranium can be partitioned among dissolved and particulate phase before being uptaken by organisms, and the chemistry of the natural waters presents a huge effect on U mobility and availability. Many analytical techniques have been employed to perform the U speciation in natural aquatic systems and to determine the so-called bioavailable forms of U. However, inconsistencies in the definition of which U fraction/species is the one bioavailable are observed. Even though studies employing biological and chemical approaches improved the knowledge about the mechanisms involved in the U uptake by organisms and the U bioavailability in natural aquatic systems, some gaps still need to be filled (e.g., considering the characteristics of tropical waters, sediments, and soils), and more studies are necessary to comprehend the whole mechanism of U uptake and the environmental and biological conditions that are involved in the U bioavailability and toxicity to aquatic organisms.

With respect to the terrestrial environments, climate strongly influences soil types, thus controlling U mobility and availability. For each soil, differences in the solubility and mobility of U as well as translocation within the plants are dominated by specific and nonspecific adsorption as well as different complexation affinities for inorganic and organic ligands, which depend mainly on the soil pH. Considering that the bioavailable fraction depends on the physicochemical characteristics of the soils, it's important to take into account soil properties, bioavailable U concentrations measured by different methods, and U accumulation in plants, when attempting to determine how soil properties influence the prediction of the bioavailable portions of U. Novel knowledge into the mechanisms controlling U mobility in tropical terrestrial systems and the prediction of U availability in soils could improve

the protection of the natural resources and contribute to the establishment of regulatory guidelines regarding the release of U in the natural systems.

Field and laboratory studies of particular sites using natural waters, aquatic organisms, sediments, soil, plants, and selective chemical extraction methods focusing on the characteristics of tropical areas may improve understanding this topic. Site-specific investigations are required in order to enable more efficient land-use planning. This is undeniably important, since each site is unique in respect of their characteristics and dynamic of environmental and geochemical processes, which have effects on the mobility of U in the soil-water-biota system.

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The Behaviour of Uranium in Soils and the Mechanisms of Its Accumulation by Agricultural Plants



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Abstract Environmental contamination by ^{238}U occurs in the resting places of rocks with high uranium content in the points, where the ground waters come out on the Earth surface. ^{238}U enters the atmosphere because of volcanic outbursts, forest fires, meteoric dust and soil transfer by the wind. A significant fraction of environmental contamination is formed by the products of ^{238}U leaching from the wastes of uranium mines and plants and releases of uranium fusion (yellow substance) from the stacks of the enterprises processing the uranium concentrate. Entrance into the environment with the wastes of phosphate industry (at phosphate rock processing), application of phosphoric fertilisers (superphosphate, precipitated phosphate and others), coil burning at thermal power plants and primary metal establishments are considered as the intensive source of agrocoenosis contamination. The conducted studies established that the accumulation of ^{238}U by crops is closely related to the content of humus, mobile calcium and physical clay in the soils. The correlation coefficient between the accumulation of ^{238}U in the oats grain and the humus content in the soil is $R = 0.91 \pm 0.04$. Differences in the accumulation of ^{238}U in plants depend on the texture of sod-podzolic soils and come up to 1.2–1.6 times. The uptake of ^{238}U from sod-podzolic soils to barley is 1.4–3.4 times higher than that of chernozem-type soils with a high content of humus and mobile calcium.

Keywords ^{238}U · Radioactive contamination · Remediation · Fertilisers · Agricultural techniques · Crops

1 Sources of ^{238}U Entrance into Agricultural Ecosystems

Uranium is a heavy natural radionuclide, participating in the formation of the Earth crust. Atomic mass of the natural uranium is 238.02891. It was discovered by the German chemist M.H. Klaproth in 1789. Uranium is widely spread in nature

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(Tananaev 2011). It was discovered in considerable concentrations in Earth material, oceans, the Earth mantle and meteorites. The half-life of ^{238}U is 4.49×10^9 years (4.49 billion years), and it is an α -emitter with maximum energy of 4.7 MeV.

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A significant fraction of environmental contamination is formed by the products of ^{238}U leaching from the wastes of uranium mines and plants and releases of uranium fusion (yellow substance) from the stacks of the enterprises processing the uranium concentrate. Entrance into the environment with the wastes of phosphate industry (at phosphate rock processing), application of phosphoric fertilisers (super-phosphate, precipitated phosphate and others), coal burning at thermal power plants and primary metal establishments are considered as the intensive source of agrocoenosis contamination (Drichko 1983). The content of mobile forms of ^{238}U in ammonium and phosphogypsum comes up to 5.95% and 23% from gross content in water-soluble form.

Uranium content in Earth crust is $2 \times 10^{-4}\%$ (Tananaev 2011). The average content of ^{238}U in all Earth soils is $2.4 \times 10^{-4}\%$ (Alexakhin 1982; Alexakhin and Korneyev 1992). The ^{238}U content in grey forest soils is equal to $3.4 \times 10^{-4}\%$, in chernozems— $3.0 \times 10^{-4}\%$, and in the upper layers of sierozemic soils of semideserts, it comes up to $2.2 \times 10^{-4}\%$. The average content of ^{238}U in soils all over the world is 24.4 Bq kg^{-1} . Global technogenic flows of ^{238}U in biosphere were approximately $1.5 \times 10^{14} \text{ Bq}$ at the operation of fuel cycle enterprises working on nuclear and fossil fuels and $1 \times 10^{14} \text{ Bq}$ at the application of phosphoric fertilisers. ^{238}U amount in ploughing horizon of agricultural areas is $1.4 \times 10^{17} \text{ Bq}$ (Alexakhin and Korneyev 1992).

Uranium belongs to the class of water migrants, and in natural media, it exists in (IV) and (VI) valency forms. In continental surface waters, the distribution of ^{238}U follows the natural and climatic zone sequence, where the concentration of this radionuclide varies from 10^{-8} to 10^{-5} g L^{-1} . In the waters of large rivers flowing through different climatic zones, the concentration of ^{238}U for the Northern Hemisphere increases from north to south (Alexakhin et al. 1990).

In natural waters, ^{238}U exists as a uranyl ion UO_2^{2+} , which forms complex compounds with inorganic and organic acids. The ability of the uranyl ion to form complexes with ions such as SO_4^{2-} , Cl^- , F^- , NO_3^- , CO_3^- , CH_3COO^- , etc. to become a part of the negatively charged colloidal sols of the hydroxide and to form complexes of uranium-organic compounds plays a major role in the migration of ^{238}U to natural waters (Drichko 1983). The forms of ^{238}U in surface waters depend on pH and the content of CO_2 and C_{org} . In neutral and slightly acidic waters of the cold and temperate zones of the humid zone, the dissolved ^{238}U migrates in the form of fulvates, hydroxy complexes or pseudocolloids. For weakly alkaline waters of the arid zone containing carbonate ion, the main forms of finding ^{238}U are stable carbonate complexes $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O}_2)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. The researchers also assume the presence of bicarbonate complex compounds ^{238}U (Alexakhin et al. 1990).

Anthropogenic sources of environmental pollution by ^{238}U , including agricultural ecosystems, are:

- Extraction of uranium in mines and a formed uranium trace
- The atomic and nuclear power industry
- Agriculture (mineral fertilisers, primarily phosphoric, may contain ^{238}U in high concentrations) and uranium content in irrigation water (Drichko 1983; Alexakhin 1982)
- The use of radioactive projectiles in military conflicts

With the systematic use of waste (phosphogypsum) and complex phosphoric fertilisers, the accumulation of gross and mobile forms of heavy natural radionuclides can occur in soils. It can reach the levels exceeding background concentrations by 1.5–2.0 times (Drichko 1983).

The nature and direction of the soil formation processes determine the distribution of uranium in the soils of certain landscape zone. These factors result in the great variety of uranium content in soils. Uranium is accumulated mainly in the sod and the upper arable soil horizon.

2 Behaviour and Forms of ^{238}U in Soils of Agricultural Lands

An important factor determining the behaviour of the ^{238}U , which enters the land cover, is its high mass concentration in the soils (Alexakhin and Korneyev 1992).

The state and fixation (sorption) of ^{238}U in soils depends on many factors (Alexakhin et al. 1990). The degree of oxidation of ^{238}U in soils is (IV) and (VI). In a highly reducing medium, ^{238}U is predominantly in 4-valence and, in oxidative, in 6-valence forms.

Sorption of ^{238}U in soils depends on the chemical properties, the physical and chemical state and concentration of elements, the granulometric and mineralogical composition of soils, the content of organic matter, the presence of certain ions in the solution, migratory-capable colloids, complexing agents, etc. (Drichko 1983; Alexakhin et al. 1990; Alexakhin and Korneyev 1992).

Soils with pH from 5 to 6 contain ^{238}U mainly in the form of well-sorbed hydrolysed forms of uranyl, and for this reason, the transition of the radionuclide into water extract from these soils is negligible. At a small (about 1 mM) content of carbonates in soil solution, hydrolysis forms of uranyl prevail in the pH range of 2–12 (Iskra and Bakhurov 1981). Therefore, even at a high pH of the solutions, the recovery of ^{238}U from the soils does not increase. Thus, at pH 11, the fraction of radionuclide that has passed from leached chernozem to water extract is only 1.5% (Iskra and Bakhurov 1981). In neutral and alkaline media, carbonate and phosphate compounds predominate (Sultanbaev and Grigoryev 1979), and this can reduce and weaken the absorption of ^{238}U in the soil (Iskra and Bakhurov 1981). At pH above 10, the equilibrium shifts again towards the formation of hydrolysis forms, and the recovery of ^{238}U decreases. In media, rich with CaCO_3 and MgCO_3 , the absorption

strength can increase due to the precipitation of $\text{Ca}_2(\text{UO}_2(\text{CO}_3)_3$ and $\text{Ca}, \text{Mg}(\text{UO}_2(\text{CO}_3)_3$). The minimum absorption of ^{238}U by sod horizons of sod-podzolic and sod-meadow soils was found at pH 2–3, maximum (97–98%) at pH 5–8 (Ovchenkov et al. 1974).

A significant concentration of humus, as a rule, increases the sorption of radionuclides in the soil (Rusanova 1971; Sultanbaev and Grigoryev 1979; Sultanbaev and Kinkalova 1979). Organic substances of the soil solution bind ^{238}U to complex compounds, differing in their solubility and stability (Manskaya et al. 1956; Evseeva et al. 1974). For example, the strength of the element complexes with humic acids is 1.5–2 times higher on average than with fulvic acids (Kichigin and Nosova 2004). Under reducing conditions at pH 5, humic acids and, at pH 6.0–6.6, fulvic acids precipitate ^{238}U , and in oxidative conditions, soluble compounds are formed. The carbonate concentration of $1 \text{ M} \times 10^{-3}$ almost eliminates the formation of soluble hydrolysis products and prevents the humate binding at the content of the humic acids lower than $0.1 \text{ M} \times 10^{-6}$. At carbonate concentrations between $5 \text{ M} \times 10^{-8}$ and $5 \text{ M} \times 10^{-4}$, the formation of uranium humates dominates (Rachkova et al. 2010). The effect of organic substances on the processes of absorption in the soil is due to the fact that they are themselves collectors of radioactive elements, or modify the absorption properties of other sorbents, and also form mobile compounds with radionuclides. Mechanisms of sorption and fixation of ^{238}U by soils have been poorly studied. Absorption process includes adsorption, ion exchange and precipitation, particularly due to oxidation-reduction reactions. Some authors (Manskaya et al. 1956; Evseeva et al. 1974) believe that the last of the above mechanisms is the most important in the process of sorption of uranium in the soil. At the same time, it was experimentally established that hexavalent uranium retains its valence in complexes with natural humic acid (Teterin et al. 2001). The mechanism of sorption consists of the exchange of hydrogen cations and uranyl UO^{2+} ; that is why the capacity and rate of absorption depend on the acidity of the medium. Fe^{3+} ions inhibit the formation of uranyl humates due to sorption on the surface of particles of colloidal humic acid (Teterin et al. 2001) that prevents the migration of ^{238}U in the form of absorbed or molecular solutions of uranyl humates. At the same time, the addition of humic acid to the hematite suspension reduces the absorption of the radionuclide; the degree of reduction depends on the pH of the medium and the amount of humic acid. In addition, the dominant factor is the fraction of ^{238}U bound to humates. In the presence of fulvates, the sorption of the radionuclide by the clayey soil components is completely inhibited (Kornilovich et al. 2001).

Sorption of ^{238}U in soil is related to the size and specific surface area of soil particles (Nikiforova 1967; Baranov and Morozova 1971; Rubtsov and Pravdina 1971; Bykova 1973; Ishchenko 1988; Ishchenko and Butnik 1990). For soil with a high content of physical clay and silt, the high values of the distribution coefficients were set (Ranson 1973; Sheppard et al. 1980; Barnett et al. 2000). The content of ^{238}U in the solid phase of clay soils is $200 - 7.9 \times 10^5$ times higher than in the equilibrium solution. For desert-sandy, meadow, meadow-swamp soils and light and typical sierozems, a direct dependence of the absorption and mobility of ^{238}U on the content of humus, potassium, calcium and physical clay has been established (Ishchenko

1988; Ishchenko and Butnik 1990). According to some estimates (Sultanbaev 1974), the content of ^{238}U in the clay fraction is up to three times higher than its concentration in unfractionated soil. At the same time, little information indicates a lack of a close relationship between the sorption of radionuclides and the granulometric composition of soils. For example, for soils in the taiga zone, up to 50% of radionuclides of the uranium series are sorbed on the surface of particles with a size of 1–100 μm , and consolidation of aggregates in this range is accompanied by a decrease in the content of radioelements (Taskaev 1979).

The strong fixation of ^{238}U in soils occurs due to its sorption by organic substances and clay minerals (illite, montmorillonite and kaolinite) (Taskaev 1979; Alexakhin et al. 1990; Rusanova 1998; Ranson 1973). Limestone weakly absorbs ^{238}U , and silicon dioxide does not absorb the uranium at all (Alexakhin et al. 1990; Savenko 2001). The sorption centres of two types are significant for sorption of radionuclides by clay minerals. These centres are located on the basal surfaces of mineral particles, where ion exchange takes place, and on the lateral faces with the formation of strong sorption complexes. According to Kornilovich et al. (2001), uranium was primarily absorbed on the lateral faces of clay minerals. The X-ray diffraction analysis (Iskra and Bakhurov 1981) showed that binding takes place according to the ion-exchange mechanism. ^{238}U competes with cations Ca^{2+} , Ba^{2+} and Mg^{2+} for sorption centres, but not with Na^+ and K^+ . According to the structural data, uranyl forms dissolved and absorbed by clay minerals are identical. In sub-acidic conditions, they correspond to the hexahydrated ion (Iskra and Bakhurov 1981). In the pH range of 6–12, the sorbed forms of uranyl are represented by UO_2OH^+ and $(\text{UO}_2)_2(\text{OH})$. Absorption of UO_2OH^+ predominates at pH 6; with a decrease in acidity, the ratio of sorption of $(\text{UO}_2)_2(\text{OH})$ increases. The isotherms of ^{238}U (VI) sorption by clay minerals have a maximum at pH 3–6 with a sharp decrease in the absorption parameters to the sides of this interval (Kornilovich et al. 2001).

The influence of the capacity of cation exchange on the sorption of ^{238}U by soils is practically absent (Bondietti and Tamura 1980). For example, the removal of organic matter and free ferrous oxides from the clayey fraction of silty loam reduces its cation-exchange capacity, without changing the absorption rate of ^{238}U . Along with this, there is an opinion (Malikov et al. 1988a) that in surface media, the Fe content controls the pH-dependent adsorption of ^{238}U . Oxide forms of metals (goethite, hematite, boehmite, etc.), on the one hand, themselves serve as sorbents of a radionuclide, and on the other, when they are adsorbed, these oxides form films on the surface of clay minerals changing their ion-exchange properties. The distribution coefficient of the radionuclide between solutions of its salts and Fe minerals reaches $2 \times 10^6 \text{ mL g}^{-1}$, which is 100 times greater than for secondary minerals.

The behaviour of ^{238}U and its forms in soils are determined both by the state of the radionuclide itself and by the physical and chemical properties of the soils. The original form of the radionuclide fallout plays an essential role in the processes of sorption and desorption of ^{238}U . For example, in 2 years later after application, the sorption of ^{238}U by five types of soil (17 soil differences) with contrasting physical and chemical properties and indicators of texture when introducing a radionuclide in the form of a solution of uranyl nitrate is 82.2–99.2% and desorption by water is

Table 1 Rate and strength of sorption of $^{238}\text{UO}_2(\text{NO}_3)_2$ in different types of soils (in relation to the original quantity), % (adopted from Alexakhin et al. 1985)

Soil type	Sorption	Desorption		
		H ₂ O	1N CH ₃ COONH ₄	2N HNO ₃
Sod-podzolic	97.0	1.7	2.4	54.6
Dark-grey forest	98.4	1.2	11.7	59.5
Grey forest	96.9	1.4	3.2	51.3
Brown forest	88.4	1.2	36.2	79.2
Chernozem				
Leached	98.5	1.2	13.4	68.4
Podzolic	82.2	5.9	24.1	51.3
Usual	85.9	7.5	9.6	57.0
Southern	90.9	3.6	25.6	68.4
Firm	98.1	1.1	22.2	76.4
Meadow chernozem	89.1	5.6	22.3	69.5
Sod	82.2	5.9	24.1	51.3
Meadow	99.2	1.5	23.6	60.8
Humic-gleyed	98.1	1.1	14.8	72.8
Meadow-swampy	87.5	3.6	23.0	69.2
Dark kastanozem	93.6	3.8	32.8	77.2
Kastanozem	87.0	4.8	40.8	61.2
Light kastanozem	87.4	4.4	26.4	72.0

1.1–7.5%, by 1N ammonium acetate solution is 2.4–40.8% and by 2N HNO₃ solution is 51.3–79.2% (Alexakhin et al. 1985) (Table 1).

The studies of Arkhipov et al. (1986) established the limits of the absolute and relative content of gross, acid-soluble and exchangeable forms of natural radionuclides (^{238}U , ^{232}Th , ^{226}Ra , ^{210}Po and ^{210}Pb) in the different types of soils of the Russian Federation. The gross content of ^{238}U is 7.4–18.5 Bq kg⁻¹ in sod-podzolic soils, 22.2–37.0 Bq kg⁻¹ in chernozems, 25.9 Bq kg⁻¹ in kastanozems, 29.6 Bq kg⁻¹ in brown semi-desert soils and 25.9 Bq kg⁻¹ in sierozems. The content of the acid-soluble forms of ^{238}U is 6–26% of the gross content, depending on the agrochemical properties of the soil. The amount of exchangeable and water-soluble forms of ^{238}U in sod-podzolic soils varies between 18% and 40%, in chernozem 9–12% of gross soil content (Arkhipov et al. 1986).

By this means, a generalisation of the accumulated data indicates that intensive and strong absorption of ^{238}U in soils occurs mainly due to organic matter and clay minerals. The processes of ion exchange, complexation, hydrolysis and oxidation-reduction designate the fixation of ^{238}U in soils.

To date, there is a lack of the investigation of the temporal aspects of ^{238}U absorption processes in various soils. The existing research methodologies do not allow to fully evaluate the transformation of forms and mechanisms of radionuclide binding in soils. One of the ways to overcome these difficulties can be carrying out complex ^{238}U full-scale and model studies (Arkhipov and Fedorova 1981).

The research of Ishchenko and Butnik (1990) conducted on different soil types in Central Asia gives a comprehensive assessment of the effect of ^{238}U on the bioavailability, depending on the time of interaction of the radionuclide with the soil.

The transformation of the ^{238}U forms in time was studied on a typical sierozem. Soil samples were taken from the plots, where cotton was grown in the first and second years and in the third year—wheat. The concentration of ^{238}U was 53 mg kg^{-1} of soil.

^{238}U from soil samples was successively extracted with distilled water, acetate-ammonium buffer solution (pH 4.8), a solution of citric acid (0.033 M), a mixture of citric (0.033 M) and oxalic (0.5 M) acids and hydrochloric acid. The content of the ^{238}U forms was calculated in %, assuming the initial value to be 100%.

It was found that uranium, introduced into the soil as a solution of $^{238}\text{UO}_2(\text{NO}_3)_2$, comprises mainly exchangeable forms with soil components in desert-sandy soil and light and typical sierozems, and in meadow soils, the uranium interaction with soil components results in acid-soluble form. From such soils as desert-sandy, light and typical sierozems, most of the ^{238}U passed into aqueous and acetate-ammonium extracts (from 48.4 to 51.5%), into which readily soluble, exchangeable compounds and organomineral complexes are displaced. There is an inverse relationship between the physical and chemical soil properties and the amount of water-soluble and exchangeable forms of ^{238}U , and with the number of fixed ^{238}U compounds, the relationship is direct. Correlation coefficients between the amount of radionuclide in water-soluble and exchangeable forms and all indicated soil parameters turned out to be rather high ($R = 0.73 - 0.88$).

The ratio of water-soluble, exchangeable, acid-soluble and fixed forms was being determined for 3 years in order to study the influence of the time factor on the transformation of the occurrence of ^{238}U in a typical sierozem; the ratio of the forms of radionuclide was determined 2 weeks after its introduction into the soil. A year later, the number of exchangeable compounds of ^{238}U increased, and the number of acid-soluble compounds decreased. After 2 years of radionuclide stay in the soil, no further changes in the content of the various forms of ^{238}U were detected. With a 3-year incubation of ^{238}U in the soil, the number of fixed compounds increased significantly in comparison with their content in the first year, while the fraction of the exchangeable forms of the radionuclide remained unchanged (Ishchenko and Butnik 1990) (Table 2). The amount of water-soluble and essentially acid-soluble forms has decreased. This occurs because acid-soluble compounds of ^{238}U have been transformed into fixed ones with time. Estimation of the removal of ^{238}U by the

Table 2 The content of various forms of ^{238}U , depending on the time of their stay in the typical sierozem, % of application

Timing of determination	Water soluble	Exchangeable	Acid-soluble	Fixed
In 2 weeks	7.5	41.5	27.6	23.8
In 1 year	5.9	47.0	21.6	25.5
In 2 years	4.1	49.1	20.8	25.6
In 3 years	2.7	47.5	10.7	39.2

above-ground mass of cotton and wheat and the estimation of the amount of radionuclide in the root system require the information on the biomass of crops. Data on the sizes of the root system remaining in the soil after harvesting cotton and wheat and the balance of the above-ground biomass could not be found.

3 Mechanisms of Transfer of ^{238}U from Soil to Plants

The role of biogenic migration of ^{238}U , when it moves in the biosphere, is very significant, although its ability to be absorbed by plants is characterised as weak (Alexakhin 1982). Nevertheless, the accumulation of ^{238}U in agricultural plants and the subsequent entrance of a radionuclide into the human body can be a source of its irradiation from the natural radiation background.

The properties of the soil-forming rock determine the content of ^{238}U in the soil; profile differentiation depends on the genetic features of soil formation (Alexakhin et al. 1990). It is noted both an accumulation of ^{238}U in the upper horizons enriched with organic substances (Sultanbaev and Grigoryev 1979) and relatively uniform distribution in the soil profile. Under pollution conditions, ^{238}U is mainly fixed by clay minerals and organic matter in the upper soil horizons (Taskaev 1979; Alexakhin et al. 1990). The initial chemical form of the element and the presence of macro-components have an effect on the sorption behaviour of the radionuclide from technogenic pollution sources. Due to the fixation (isomorphic entry into the crystal lattice of minerals, diffusion into the internal cavities of the mineral structure by its defects, precipitation or co-precipitation, complexation with nonmobile fractions of organic matter), the biological availability of the radionuclide in contaminated soils may be lower than in the background ones. A similar fact has been established for the mountain taiga soils of Yakutia, altered as a result of exploration and development of ^{238}U deposits (Sobakin 1998). It was found that the biological absorption coefficient (BAC) of ^{238}U correlates most closely with the content of the acid-soluble form of the element.

The main factors determining the intake of ^{238}U from soil to plants are:

- The concentration of ^{238}U
- Biological features of plants
- Physical and chemical indicators of soils
- The content of ^{238}U mobile forms in the soil
- The chemical composition of soils and plants, soil moisture, the granulometric and mineralogical composition of the soil, the time of interaction with the soil and the forms of deposition of ^{238}U on the soil and vegetation cover

The quantitative characteristics of radionuclide intake from soil to plants are:

- Accumulation coefficient AC (Alexakhin and Korneyev 1992)

$$\text{AC} = \frac{\text{Radionuclide concentration in the plant (dry weight)}}{\text{Radionuclide concentration in the soil}}$$

- Biological absorption coefficient *BAC* (Alexakhin and Korneyev 1992)

$$\text{BAC} = \frac{\text{Radionuclide concentration in the plant ash}}{\text{Gross radionuclide concentration in the soil}}$$

When oats were cultivated on different soils of the non-chernozem zone of the Russian Federation, where ^{238}U was introduced as a solution of uranyl chloride with concentrations of 25 and 50 mg kg $^{-1}$ of soil, the negative effect of the radionuclide on the growth, development and formation of plant productivity was not established. The primary amount of ^{238}U in sod-podzolic, grey forest soils and chernozems is in the exchangeable state (40–70%), which determines the high values of AC of ^{238}U for oats grain and straw (Table 3). The acid-soluble fraction of soil is important on typical sierozem, and the content of the exchange fraction on sod-podzolic, grey forest soils and chernozems plays a leading role in the intake of ^{238}U from the soil into the plants.

Mordberg et al. (1976) studied the effect of various concentrations of ^{238}U on the growth and yield of plants on the example of corn on leached chernozem in the North Caucasus. It was found that concentrations of ^{238}U exceeding 2.5 kBq kg $^{-1}$ (200 mg kg $^{-1}$ of soil) caused growth inhibition and a decrease in yield due to the toxic effect of the radionuclide on the development of the root system. Depending on the physical and chemical properties of the soils, the degree of the growth inhibition of corn plants was different, and the weight of plants when introducing ^{238}U into the soil ranged from 14% to 21% in comparison with the control (Mordberg et al. 1976). The accumulation of ^{238}U by barley, oats and vetch plants on sod-podzolic soil containing 10, 100, 500 and 1000 mg kg $^{-1}$ was to a certain level in a direct but not proportional dependence on the concentration of ^{238}U in the soil. In the range of very high concentrations in the soil (over 500 mg kg $^{-1}$), the accumulation of ^{238}U by

Table 3 Accumulation coefficients of ^{238}U in the yield of oats on different soils' greenhouse experiment, AC of ^{238}U (Bq kg $^{-1}$ plant dry weight) (Bq kg $^{-1}$ soil) $^{-1}$

Soil	$^{238}\text{U} - 312.5 \text{ Bq kg}^{-1}$ of soil				$^{238}\text{U} - 625 \text{ Bq kg}^{-1}$ of soil			
	Weight, g pot $^{-1}$		AC ^{238}U , n × 10 $^{-3}$		Weight, g pot $^{-1}$		AC ^{238}U , n × 10 $^{-3}$	
	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw
Sod-podzolic sandy loam	20.6	27.4	2.92	20.0	21.2	26.5	2.85	20.2
Sod-podzolic sandy loam	13.2	26.1	4.08	23.9	14.9	25.4	3.97	24.5
Sod-podzolic medium loamy	17.2	22.7	3.48	25.4	18.3	24.2	3.23	23.3
Sod-podzolic medium loamy	16.7	23.9	3.15	24.6	17.1	25.8	3.32	22.0
Sod-podzolic medium loamy	15.9	27.0	3.00	20.2	16.2	28.2	2.90	18.2
Grey forest medium loamy	19.4	28.4	2.20	15.8	20.3	29.7	2.32	16.4
Chernozem leached medium loamy	21.8	30.5	1.49	9.4	22.0	31.0	1.53	9.6

plants reached a constant value and did not increase at a concentration of 1000 mg kg⁻¹ (Zimakov and Lazarev 1984). Malikov et al. (1988b) studied on leached chernozem and noticed an increase in the concentration of ²³⁸U in the soil from 100 to 500 mg kg⁻¹ caused an increase in AC of ²³⁸U for alfalfa, Sudan grass and roots of red and sugar beet by a factor of 1.8–4.7 and had practically no effect on the accumulation of uranium by peas, cucumbers and tomatoes.

The data of the greenhouse experiment with spring barley on sod-podzolic medium loamy soil contaminated with UO₂(NO₃)₂ × 6H₂O showed that at a ²³⁸U concentration of 150 mg kg⁻¹ of soil, there was a detectable inhibition of barley plants, which appeared in a 1.2-fold decrease in growth in comparison with the control. The decrease in the biomass of barley straw at a concentration of ²³⁸U of 100–150 mg kg⁻¹ of soil was 1.5–2.0 times, and the mass of grain decreased by a factor of 1.2. The levels of radionuclide content in barley straw were 2.5–8.0 times higher than in grain. Application of the modified diatomite-based sorbent in an amount of 0.5 g kg⁻¹ to the soil containing 100 mg kg⁻¹ of ²³⁸U reduced the accumulation of radionuclide by barley straw in average by 10% (Kulyeva and Kasyanenko 2009).

The process of intake of ²³⁸U in plants occurs continuously throughout the entire vegetation period, and plants accumulate the radionuclide per unit mass in the earlier phases of their development more than in later phases (Ratnikov et al. 2007). The largest amount of ²³⁸U in plants accumulates in the earing phase of oats and barley (Ratnikov et al. 2007) (Table 4).

Over the time, the physical and chemical state and strength of ²³⁸U fixation in radioactively contaminated soils may change. Thus, in model-field experiments, it was found that the biological absorption of a radionuclide depends on its initial

Table 4 The concentration of ²³⁸U in oat and barley plants during the vegetation period, Bq kg⁻¹ dry weight

Types of soils	Oats		Barley	
	20-day plants	Vegetative mass after 45 days	20-day plants	Vegetative mass after 45 days
Sod-podzolic sandy loam (Vladimir region)	6.0	13.2	4.7	10.2
Sod-podzolic sandy loam (Moscow region)	9.8	22.7	6.5	15.1
Sod-podzolic medium loamy (Kaluga region)	6.9	10.8	5.2	8.4
Grey forest medium loamy (Kaluga region)	5.3	9.2	4.2	7.0
Leached chernozem (Tula region)	4.5	7.1	3.1	5.9

Greenhouse experiment (Adopted from Kulyeva and Kasyanenko 2009)

chemical form for another 2 years after radioactive contamination of the meadow sod surface. The bioavailability of ^{238}U , which entered the soil in the form of ammonium diuranate, uranyl chloride, uranium (VI) oxide, uranium (IV, VI) oxide, uranyl sulphate, sodium uranate and uranium (IV) oxide, consistently decreases. For the third year after the contamination, these differences become even (Ivanov and Yudintseva 1987).

Peculiarities of mineral nutrition, different duration of the growing season, the character of the distribution of root systems in the soil, differences in productivity and other biological features of plants affect the accumulation of radionuclides by different species and varieties of crops. Accumulation of ^{238}U in plants varies from 1.5 to 70 times depending on their specific features (Kuznetsov et al. 1986) (Table 5). The accumulation coefficients are minimal for the economically valuable parts of the crop.

Uranium-238 in the soil, when it enters the plants, accumulates in the root system, which serves as a barrier to the transport of the radionuclide into the above-ground mass of plants. Accumulation of ^{238}U by vegetative mass of plants is 1.5–10 times higher than accumulation by generative organs (Iskra and Bakhurov 1981;

Table 5 Accumulation coefficients of heavy natural radionuclides in crops, (Bq kg^{-1} of plant dry weight) (Bq kg^{-1} of soil) $^{-1}$, $n \times 10^{-2}$

Crop, part of the yield	^{232}Th	^{238}U
Winter rye		
Grain	0.56	0.56
Straw	1.05	2.13
Spring wheat		
Grain	0.30	0.83
Straw	1.15	3.24
Barley		
Grain	0.53	0.7
Straw	1.30	2.50
Oats		
Grain	0.50	0.90
Straw	1.56	4.91
Potatoes		
Tubers	0.98	1.58
Tops	7.96	12.70
Sugar beet		
Roots	1.70	13.50
Tops	9.68	38.60
Annual cultivated grasses	2.84	3.73
Perennial cultivated grasses	3.27	6.36
Motley grasses	3.53	6.94
Clover	2.41	3.92
Alfalfa	0.97	9.50
Corn green material	1.51	3.32

Table 6 The accumulation coefficients of ^{238}U by different crops, AC of ^{238}U (Bq kg^{-1} of plant dry weight) (Bq kg^{-1} of soil) $^{-1}$

Crop	AC ^{238}U , $n \times 10^{-3}$	References	Crop	AC ^{238}U , $n \times 10^{-3}$	References
Wheat	0.4–1.0	Mordberg et al. (1976)	Potatoes	0.1–2.0	Mordberg et al. (1977)
	3.8	Mordberg et al. (1976)	Beet	0.2–3.0	Mordberg et al. (1977)
	0.85	Mordberg et al. (1980)	Cabbage	0.6	Mordberg et al. (1977)
Barley	0.16	Sultanbaev and Grigoryev (1979)	Tomatoes	0.3–0.7	Mordberg et al. (1977)
	0.28–1.72	Sultanbaev and Grigoryev (1979)	Cucumbers	0.3	Mordberg et al. (1977)
Rye	0.36	Sultanbaev and Grigoryev (1979)	Pumpkin	0.3–0.7	Mordberg et al. (1977)
Corn	1.7	Mordberg et al. (1976)	Watermelon	0.5–2.0	Mordberg et al. (1977)
Millet	0.9–1.6	Mordberg et al. (1976)	Melon	0.7–2.0	Mordberg et al. (1977)
Buckwheat	4.4	Mordberg et al. (1976)	Sunflower	2.7	Mordberg et al. (1977)
Peas	0.1–3.0	Mordberg et al. (1976)	Walnut	0.16–1.44	Sultanbaev and Grigoryev (1979)
	0.54	Mordberg et al. (1976)			

Drichko 1983; Alexakhin et al. 1990; Alexakhin and Korneyev 1992). Table 6 summarises data from various sources on AC of ^{238}U in cereals, legumes, technical crops and vegetables.

As it could be seen from Table 6, buckwheat has the highest uranium accumulation ability, and rye has the lowest one in comparison to the other cereals and leguminous and industrial crops. Among vegetable and fruit crops, the minimum AC for ^{238}U is observed in cucumbers, cabbage, tomatoes and pumpkin, maximum in sunflower. The high content of ^{238}U is noted in the beetroots and potato tubers (Mordberg et al. 1977). The ^{238}U accumulated by the plants is concentrated to a greater extent in the vegetative mass, but the ratio between the radionuclide concentrations in the vegetative mass and the reproductive organs for each crop is different. In cereal crops, as a rule, the radionuclide accumulates in the vegetative mass. The AC of ^{238}U in grain and straw of winter wheat on different types of soils, according to Stasyev (1986), ranges from 0.0004 to 0.003 and from 0.002 to 0.006, respectively. ^{238}U AC for the corn is 0.0001–0.012.

According to the results of experiments on sod-podzolic and peat soils in Belarus, the AC of ^{238}U in vegetable products increases in the following order: cucumber and zucchini (0.8–2.3); cabbage, potatoes, beets and parsley (4.0–5.7); and tomato, carrots and dill (18.0), $n \times 10^{-4}$, respectively. It is shown that ^{238}U from soils, which are close in their characteristics, is more likely to enter vegetables than corn kernels (Sokolik et al. 2013).

Malikov et al. (1988b), based on the generalised data of laboratory and greenhouse experiments on the ^{238}U transfer in the yield of various crops on leached chernozem in the North Caucasus, distinguished the following series of crops by the accumulation of ^{238}U in the economically valuable organs of plants: sugar beet > red

beet > cucumbers > tomatoes. AC of ^{238}U for fodder crops increases in the following order: corn (for silage) > vegetative mass of peas > alfalfa (hay) > Sudan grass (hay).

It is known that in addition to specific features, the variety of crops influences the transfer of ^{238}U into plants. For example, the difference in the content of ^{238}U in spring wheat straw grown on typical sierozem, depending on the variety, was 2.5 times, and in grain, it was 2.4 times (Butnik et al. 1989).

The main factor affecting the uranium transfer from the soil to the plants is the agrochemical properties and humidity of contaminated soils. The type, hydromorphic feature and acidity of the soil medium significantly affect the plant uptake of ^{238}U from the soil. The transfer of ^{238}U from hydromorphic peat soil into the vegetation of the same species is more intensive than from automorphic sod-podzolic soil. This is evidenced by higher transfer factors of ^{238}U into corn grain from peat soil than from sod-podzolic soils. More intensive accumulation of ^{238}U from peat soil is also facilitated by its higher acidity ($\text{pH}_{\text{KCl}} 5.8$) compared to sod-podzolic soil ($\text{pH}_{\text{KCl}} 7.3$) (Sokolik et al. 2013).

Our investigations under conditions of greenhouse experiments on two soil types (seven soil differences) showed that the accumulation of ^{238}U in the yield of oats, barley, spring wheat and peas depends on agrochemical characteristics of soils. The AC of ^{238}U in the grain of oats is $(1.5\text{--}4.1) \times 10^{-3}$ and in straw $(9.4\text{--}25.0) \times 10^{-3}$. The AC of ^{238}U in the pea grain is $(0.8\text{--}3.3) \times 10^{-3}$ and in its straw $(7.1\text{--}18.3) \times 10^{-3}$. The accumulation of ^{238}U by the grain of spring wheat and barley on leached chernozem is 3.7–4.4 times lower than on sod-podzolic sandy loam soil. Not all properties of soils equally influenced the rate of ^{238}U accumulation in the crops. The closest inverse relationship was found between the accumulation of a radionuclide in the grain and the content of humus in the soil. The correlation coefficient between the accumulation of ^{238}U in the oats grain and the humus content in the soil was $R = 0.91 \pm 0.004$. Soils rich in humus and containing a significant amount of Ca^{2+} ions in soil absorbing complexes (SAC) have a maximum absorption capacity and are characterised by a heavier granulometric composition. The solid phase of such soils absorbs radionuclides, and a smaller proportion of them pass into plants in comparison with soils, which have lower fertility (Ratnikov et al. 2007).

Under the greenhouse experiment conditions for five types of soils, the ACs of ^{238}U for barley varied up to eight times, depending on the soil agrochemical properties. With an increase in the humus content in the soil, exchangeable calcium and the reaction of the soil solution became neutral, and the ACs of natural radionuclides decreased in most cases. The relationship between the AC of natural radionuclides in barley plants and the indicated soil properties in most cases was statistically significant and could be described by equations of curvilinear regression calculated on the basis of experimental data (Arkhipov et al. 1984).

Depending on the agrochemical, physical and chemical properties of the soils of the North Caucasus, the accumulation coefficient of uranium by pea grain varied within the limits of $(10\text{--}181) \times 10^{-4}$, and by the vegetative mass, it varied within $(9\text{--}134) \times 10^{-3}$. The mobility of uranium in soils and the soil-plant system changed during the transition from acidic soils to neutral and slightly alkaline soils.

Correlation coefficients between the volume of the uranium accumulation in the grain and the vegetative mass of peas and the soil pH were 0.480 and 0.739, respectively. The increase in the migration capacity of uranium under alkaline conditions was associated with the formation of soluble uranyl carbonate complexes (Malikov et al. 1988b).

To date, information on the effect of various quantities and types of mineral fertilisers on the transfer of ^{238}U to crops is not enough, and the results obtained in greenhouse experiments cannot be recommended for use in the field. According to the work of Malikov et al. (1988b), in the conditions of greenhouse experiment, it was established that the application of compound mineral fertiliser and various combinations of nitrogen, phosphorus and potassium on the leached chernozem of the North Caucasus raised the accumulation of ^{238}U in the grain of spring wheat by 1.1–1.4 times. In the field, the application of mineral and organic fertilisers on typical sierozem, both in their combination and separately, significantly reduced the intake of the radionuclide in the yield of oats, barley and cotton by a factor of 1.5–3.

4 The Results of Experimental Studies on the Accumulation of ^{238}U in the Yield of Cereals on Different Soils with the Application of Mineral Fertilisers and Ameliorants

Factors influencing the transfer of heavy natural radionuclides into plants are their physical and chemical properties, concentrations in the soil, agrochemical properties of soils, biological features of plants and natural and climatic conditions for cultivating crops on contaminated lands.

An experimental evaluation of the influence of agrochemical techniques of cultivating grain crops (oats and barley) on the intake of ^{238}U into plants and accumulation in the yield was carried out on different soils of the non-chernozem zone of Russia under the field conditions in microplot tests. In the field, the influence of a compound mineral fertiliser on the accumulation of ^{238}U in the barley crop on two soil types (seven soil varieties) was studied. Studies on the effect of various quantities of mineral fertilisers, lime and humus on the productivity of oats and barley, the entrance of ^{238}U into the plant and its removal at harvesting were carried out on sod-podzolic sandy loam soil. ^{238}U was applied to the soil surface in a soluble form of uranyl chloride, and then the soil was trenched on the ploughing depth of 0–20 cm. The soil contamination density of ^{238}U in all experiments was 187.5 kBq m^{-2} . Oats and barley were cultivated according to a typical flow process chart. The seeds in all the experiments were planted in rows. Harvesting was carried out in a phase of full ripeness. The content of ^{238}U in soils before the experiments' establishment was $17.5\text{--}38.5 \text{ Bq kg}^{-1}$, depending on the soil properties.

After the harvest, soil and plant (grain and straw) samples were taken to determine their contents of ^{238}U . Uranium in soil was determined by the photometric method with arsenazo III (Savvin 1971). Neutron activation analysis on ^{238}U determined its content in plant samples after their drying and grinding and after the irradiation with above-thermal neutrons in the integral flux $(0.3\text{--}1.2) \times 10^{15}$ neutrons cm^{-2} .

Aggregated transfer factor (TF), the calculated value, was used as the parameter of ^{238}U transfer to crops:

$$\text{TF} = \frac{\text{The concentration of } ^{238}\text{U in the air dry weight of plants, Bq kg}^{-1}}{\text{Soil contamination density of } ^{238}\text{U, kBqm}^{-2}}$$

4.1 *The Effect of Mineral Fertilisers on the Accumulation of ^{238}U in the Barley Crop on the Main Types of Soils of the Non-chernozem Zone*

An experiment with spring barley to study the effect of mineral fertilisers on the accumulation of ^{238}U in the crop was carried out in model-field conditions in plastic boxes ($50 \times 50 \times 50$ cm) without a bottom on sod-podzolic soils of different textures and varying degrees of cultivation (No. 1–5), grey forest soils (No. 6) and leached chernozem (No. 7). Agrochemical characteristics of soils are presented in Table 7. The soil for field experiments was selected from the arable layer (0–25 cm) in the aligned areas, where cereal crops were cultivated with the application of mineral

Table 7 Agrochemical properties of soils

No.	Soil	pH_{KCl}	Humus, %	P_2O_5	K_2O	Hydrolytic acidity	Ca	Mg
				mg kg^{-1} of soil	$\text{mg-eq (100 g of soil)}^{-1}$			
1	Sod-podzolic sandy loam (Vladimir region)	5.6	1.0	97	83	1.2	3.2	0.3
2	Sod-podzolic sandy loam (Moscow region)	4.3	1.1	77	37	4.8	2.5	0.2
3	Sod-podzolic medium loamy (Moscow region)	4.5	1.2	101	88	4.4	7.6	0.8
4	Sod-podzolic medium loamy (Kaluga region)	5.2	1.5	145	120	2.9	8.9	0.9
5	Sod-podzolic medium loamy (Moscow region)	5.6	2.2	129	108	1.9	7.5	0.8
6	Grey forest medium loamy (Kaluga region)	5.4	2.2	138	108	1.2	14.0	8.5
7	Leached medium loamy chernozem (Tula region)	5.3	5.1	153	126	0.95	17.5	9.7

fertilisers in recommended quantities for the given zone, at the farms of Vladimir (soil No. 1), Moscow (soil No. 2, 3, 5), Kaluga (soil No. 4, 6) and Tula (No. 7) regions. ^{238}U was introduced into the soil in the form of a solution of uranyl chloride; the soil was thoroughly mixed with the solution in a separate container and then placed into the boxes. The experimental alternatives are (1) control (background) without fertilisers and (2) application of a compound mineral fertiliser— $\text{N}_{100}\text{P}_{100}\text{K}_{100}$. Mineral fertilisers were applied as NPK. The number of replications in the experiment was 4.

The entrance of ^{238}U to plants and its accumulation in barley grain and straw both in the control variant and at the application of mineral fertilisers depended on the type of soils (Table 8). On unfertilised sod-podzolic soil, the TF of ^{238}U for grain was 1.4–3.4 times, and for straw, it was 1.2–2.7 times higher than for soils of the chernozem type. The same pattern was noted at the application of mineral fertilisers: the accumulation of ^{238}U in barley grain on sod-podzolic soils was 1.5–3.3 times higher than on grey forest soil and leached chernozem. The greatest amount of ^{238}U in the barley harvest was accumulated on sod-podzolic sandy loam soil: the concentration of ^{238}U in grain was 1.67–2.19 Bq kg^{-1} , and in straw, it was 12.4–13.1 Bq kg^{-1} (dry weight). When barley was grown on unfertilised sod-podzolic medium loamy soil, the content of ^{238}U in grain was 1.3–1.9 times lower than in the case of sod-podzolic sandy loam soil. Differences in the accumulation of ^{238}U in straw depended on the texture of sod-podzolic soils and came up to 1.2–1.6 times. On well-cultivated soil with a high content of humus and calcium and high absorption capacity, the smallest accumulation of ^{238}U in the barley crop was noted even without any additional application of mineral fertilisers: the TF of ^{238}U for grain on leached chernozem was 1.8–2.7 times lower than on sod-podzolic sandy loam soils.

Table 8 Accumulation of ^{238}U in the yield of barley on different soils in the case of application of mineral fertilisers, TF of ^{238}U (Bq kg^{-1} of plant dry weight) (kBq m^{-2}) $^{-1}$; microfield experiment

Soil	Part of the harvest	TF ^{238}U , $n \times 10^{-3}$	
		Without fertilisers	$\text{N}_{100}\text{P}_{100}\text{K}_{100}$
Sod-podzolic sandy loam (Vladimir region)	Grain	8.94	6.45
	Straw	65.8	52.2
Sod-podzolic sandy loam (Moscow region, Lyubertsy)	Grain	11.7	7.96
	Straw	70.0	53.3
Sod-podzolic medium loamy (Moscow region, Ramenskoye)	Grain	6.94	5.88
	Straw	49.8	45.3
Sod-podzolic medium loamy (Kaluga region)	Grain	9.33	7.46
	Straw	52.9	43.3
Sod-podzolic medium loamy (Moscow region, Dolgoprudny)	Grain	6.20	5.14
	Straw	43.2	38.6
Grey forest medium loamy (Kaluga region, Vorotynsk)	Grain	4.54	3.49
	Straw	35.5	23.7
Leached medium loamy chernozem (Tula region, Plavsk)	Grain	3.47	2.43
	Straw	25.5	18.5

The application of a compound mineral fertiliser to sod-podzolic sandy loam soil provided a reduction in the content of ^{238}U by 1.4–1.5 times in barley grain and by 1.3 times in straw. This was due to the recharge of phosphorus and potassium in the soil and a balanced application of nitrogen. The TF of ^{238}U (Bq kg^{-1} of grain) (kBq m^{-2}) $^{-1}$ on sod-podzolic medium loamy soils with the application of mineral fertilisers was $(5.1 - 7.5) \times 10^{-3}$, which is 1.2 times lower than on control. Under the same conditions of cultivation of barley on sod-podzolic medium loamy soils, it is possible to obtain grain and coarse fodder with a lower content of ^{238}U in comparison with sod-podzolic soils. The high efficiency of mineral fertilisers was noted to reduce the transfer of ^{238}U to barley on grey forest soil and leached chernozem. The smallest quantity of ^{238}U in barley grain and straw accumulates when applying mineral fertilisers to leached chernozem. The effectiveness of mineral fertilisers in reducing the accumulation of ^{238}U in barley yield grown on leached chernozem was 1.3–1.4 times higher than on grey forest soil.

4.2 Influence of Mineral Fertilisers and Ameliorants on the Accumulation of ^{238}U in the Cereal Crops

The experimental evaluation of the influence of lime, mineral and organic fertilisers on the entrance of ^{238}U into oats and barley was carried out under conditions of microplot field experiments on sod-podzolic sandy loam soil. The following are the agrochemical characteristics of the soil before the establishment of the experiments: the humus content was 0.98%; pH_{KCl} was 4.1; hydrolytic acidity was 4.5 mg-eq (100 g of soil) $^{-1}$; Ca content was 1.7 mg-eq (100 g of soil) $^{-1}$; and the content of mobile phosphorus and exchangeable potassium was 78 and 51 mg kg^{-1} , respectively.

Ameliorants (lime and humus) were applied in accordance with the experience scheme in the autumn, and mineral fertilisers in the form of NPK were applied in spring. ^{238}U was introduced into the soil in the form of uranyl chloride, in concentration 50 mg kg^{-1} of soil or 625 Bq kg^{-1} . The plot area was 1 m^2 , and the number of replications in the experiment was 4. Flexible PVC, which was dug into the ground, contoured each plot in order to eliminate the horizontal migration of ^{238}U . The protective zone between the plots was 2 m.

The negative effect of ^{238}U with the contamination density of sod-podzolic sandy loam soil 187.5 kBq m^{-2} on the growth and development of oats and barley did not appear. In the control variant, the growth inhibition of plants, mainly barley, was noted due to the reduced supply of plants with nitrogen, phosphorus and potassium, which led to the low grain yield of the crops.

Application of mineral fertilisers to the sod-podzolic sandy loam soil in a dose of $\text{N}_{80}\text{P}_{80}\text{K}_{80}$ facilitated the reduction of the content of ^{238}U by 1.2 times in the oats grain and by 1.5 times in the oats straw in comparison with the control (Table 9).

The use of mineral fertilisers for oats in the ratio N:P:K = 1:3:1 provided a reduction of the accumulation of ^{238}U in the crop by a factor of 1.5–1.7. When potassium fertilisers were applied in an increased dose (K_{240} kg of a.i. per ha), the concentration of ^{238}U in grain was 1.2 times lower than in the case of application of $\text{N}_{80}\text{P}_{80}\text{K}_{80}$. Liming of the sod-podzolic sandy loam soil reduced the accumulation of ^{238}U in the oats grain by 2.1 times in comparison with the control. The maximum positive effect on limiting the transfer of ^{238}U from soil into oat plants and the reduction of the accumulation in oats yield was obtained in a variant with co-application of humus and $\text{N}_{80}\text{P}_{80}\text{K}_{80}$; in this case, the content of radionuclide in the grain of oats was 2.5 times and in straw 2 times lower than when using only mineral fertilisers.

Agrochemical techniques in technologies of cultivation of crops on radioactively contaminated lands facilitated the increase in their productivity, which could lead to an increase in the removal of radionuclides with yield (Sanzharova et al. 2010).

The removal of ^{238}U with oats grain increased by 1.4–1.5 times in the case of the application of mineral fertilisers if it was compared with the ^{238}U in the control samples. The lime application on the background of $\text{N}_{80}\text{P}_{80}\text{K}_{80}$ led to the larger decrease in the removal of ^{238}U with grain yield from a unit area compared to the version with mineral fertilisers, but the differences are not reliable. The removal of ^{238}U with grain yield in the case of combined application of mineral fertilisers and humus decreased by 1.4 times in contrast with $\text{N}_{80}\text{P}_{80}\text{K}_{80}$. The use of ameliorants (lime and humus) on soil contaminated with ^{238}U led to a decrease in radionuclide removal by oat straw from the soil by a factor of 1.4–1.7 and in variants with mineral fertilisers was by a factor of 1.1 (Table 9).

When barley was cultivated on sod-podzolic sandy loam soil, the application of compound mineral fertiliser ($\text{N}_{80}\text{P}_{80}\text{K}_{80}$) reduced the accumulation of ^{238}U in the crop by 1.3–1.5 times (Table 10). The content of ^{238}U in barley grain, when a higher dose of phosphorus (P_{240}) or potassium (K_{240}) was included in the compound mineral fertiliser, decreased by 1.6–1.8 times compared to the control. The concentration of ^{238}U in barley grain with the introduction of phosphorus in a dose of 240 kg of active ingredient per 1 hectare decreased by 1.2 times compared to variant of $\text{N}_{80}\text{P}_{80}\text{K}_{80}$. The application of an increased dose of potassium fertilisers on the background of the $\text{N}_{80}\text{P}_{80}$ limited the uptake of ^{238}U by barley up to 1.4 times.

Table 9 Accumulation of ^{238}U in the yield of oats grown on sod-podzolic sandy loam soil

Experimental alternative	Yield, g m ⁻²		Concentration of ^{238}U , Bq kg ⁻¹		Removal of ^{238}U , Bq m ⁻²	
	Grain	Straw	Grain	Straw	Grain	Straw
Without fertilisers	114	283	2.16	18.4	0.25	
$\text{N}_{80}\text{P}_{80}\text{K}_{80}$	213	369	1.78	12.2	0.38	
$\text{N}_{80}\text{P}_{240}\text{K}_{80}$	239	412	1.48	11.1	0.35	
$\text{N}_{80}\text{P}_{80}\text{K}_{240}$	272	483	1.33	10.2	0.36	
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{CaCO}_3, 4 \text{ t ha}^{-1}$	319	491	1.04	7.7	0.33	
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{humus}, 30 \text{ t ha}^{-1}$	393	520	0.71	6.1	0.28	

Table 10 Accumulation of ^{238}U in the yield of barley grown on sod-podzolic sandy loam soil

Experimental alternative	Yield, g m ⁻²		Concentration of ^{238}U , Bq kg ⁻¹		Removal of ^{238}U , Bq m ⁻²	
	Grain	Straw	Grain	Straw	Grain	Grain
Without fertilisers	90	194	1.81	16.0	0.16	
$\text{N}_{80}\text{P}_{80}\text{K}_{80}$	202	375	1.36	10.6	0.27	
$\text{N}_{80}\text{P}_{240}\text{K}_{80}$	234	419	1.13	9.2	0.26	
$\text{N}_{80}\text{P}_{80}\text{K}_{240}$	253	394	0.98	7.7	0.25	
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{CaCO}_3, 4 \text{ t ha}^{-1}$	279	442	0.70	6.6	0.20	
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{humus}, 30 \text{ t ha}^{-1}$	314	481	0.58	4.9	0.18	

Table 11 The efficiency of mineral fertilisers and ameliorants in the cultivation of oats and barley on sod-podzolic sandy loam soil containing ^{238}U . TF ^{238}U (Bq kg⁻¹ of grain) (kBq m⁻²)⁻¹

Experimental alternative	Oats		Barley		Ratio of decrease, times	
	TF ^{238}U , n × 10 ⁻³	Ratio of decrease, times	TF	V		
				TF	V	
Without fertilisers	11.7	1.0	1	9.6	1.0	1.0
$\text{N}_{80}\text{P}_{80}\text{K}_{80}$	9.6	1.2	0.6	7.2	1.3	0.6
$\text{N}_{80}\text{P}_{240}\text{K}_{80}$	8.0	1.5	0.7	6.0	1.6	0.6
$\text{N}_{80}\text{P}_{80}\text{K}_{240}$	7.2	1.6	0.7	5.2	1.8	0.7
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{CaCO}_3, 4 \text{ t ha}^{-1}$	5.6	2.1	0.8	3.7	2.6	0.9
$\text{N}_{80}\text{P}_{80}\text{K}_{80} + \text{humus}, 30 \text{ t ha}^{-1}$	3.9	3.0	0.9	3.1	3.1	0.9

In the case of the soil liming, the accumulation of ^{238}U in the barley yield was 2.4–2.6 times lower than that in the control. The introduction of humus into sandy loam soil on the background of mineral fertilisers provided the production of barley grain with the smallest content of ^{238}U . The TF of ^{238}U in barley grain with the combined use of organic and mineral fertilisers was reduced by 2.4 times in comparison with the separate application of mineral fertilisers (Table 11).

The application of mineral fertilisers during the cultivation of spring barley on sod-podzolic sandy loam soil increased the yield of grain by 2.2–2.8 times and the removal of ^{238}U with grain by 1.4–1.6 times. In the experiment with application of fertilisers in the dose $\text{N}_{80}\text{P}_{80}\text{K}_{80}$, there was the maximal removal of ^{238}U (Bq m²)⁻¹ with barley yield. The effectiveness of liming in reducing the carry-over of ^{238}U with barley yield was 1.4 times as compared with the application of a single dose of mineral fertilisers. Removal of ^{238}U with barley yield decreased by 1.7 times during the soil cultivation with the application of humus and $\text{N}_{80}\text{P}_{80}\text{K}_{80}$ in comparison with a variant of just $\text{N}_{80}\text{P}_{80}\text{K}_{80}$ (Table 10).

A comparative assessment of the effectiveness of the application of agrochemical techniques on sod-podzolic sandy loam soil showed that when mineral fertilisers were applied in the dose $\text{N}_{80}\text{P}_{80}\text{K}_{80}$, the transfer of ^{238}U into the grain of oats and barley decreased by 1.2–1.3 times in comparison with the control (Table 11). Increase in the dose of phosphorus fertilisers (P_{240}) in the compound mineral fertiliser led to a decrease in the accumulation of ^{238}U in the grain of oats and barley by

a factor of 1.2 compared to a single dose of $N_{80}P_{80}K_{80}$. The application of an increased dose of potassium (K_{240}) provided a more significant positive effect on limiting the uptake of ^{238}U by barley than its application when cultivating oats. Accumulation of ^{238}U decreased 2.1 times in oats grain and 2.6 times in barley grain in the case of the decrease in acidity of the soil solution due to the application of 4 tons per ha of $CaCO_3$.

The maximum positive effect on the reduction of the accumulation of ^{238}U in the grain of oats and barley on sod-podzolic sandy loam soil was obtained in the case of the introduction of humus on the background of $N_{80}P_{80}K_{80}$ (Table 11). Under the same conditions of cultivation of grain crops, the TF of ^{238}U for oats grain was 1.2–1.5 times higher than the TF of ^{238}U for barley grain. The removal of ^{238}U with the grain of oats and barley increased by 1.1–1.6 times in the case of the application of mineral fertilisers if compared with the control.

5 Conclusions

As a result of the conducted studies, it was established that the accumulation of ^{238}U by crops is closely related to the content of humus, mobile calcium and physical clay in the soils. The correlation coefficient between the accumulation of ^{238}U in the oats grain and the humus content in the soil was $R = 0.91 \pm 0.04$. The differences in the accumulation of ^{238}U in plants depended on the texture of sod-podzolic soils and came up to 1.2–1.6 times. The uptake of ^{238}U from sod-podzolic soils to barley was 1.4–3.4 times higher than that of chernozem-type soils with a high content of humus and mobile calcium.

A directly proportional relationship was established between the accumulation coefficient of ^{238}U for barley and oats and the radionuclide content in the soil, coming up to 100 mg kg^{-1} . At a concentration of ^{238}U over 150 mg kg^{-1} of sod-podzolic soil, the radionuclide had a negative effect on the development of the root system, which resulted in a decrease of the barley grain yield by a factor of 1.2 in comparison with the control. The accumulation coefficient of ^{238}U for barley decreased with the increase of radionuclide concentration up to 200 mg kg^{-1} .

The maximum quantity of ^{238}U accumulates in the root system, and this serves as a barrier to the transport of the radionuclide into the above-ground mass of plants. Accumulation of ^{238}U by vegetative mass of plants was 1.5–10 times higher than accumulation by generative organs.

Accumulation of ^{238}U in plants varies from 1.5 to 70 times depending on their specific features. The accumulation coefficient of ^{238}U by the economic-valuable part of the yield of different crops grown on sod-podzolic medium loamy soil was in the following order: oats, 3.2×10^{-3} ; peas, 2.2×10^{-3} ; barley, 1.9×10^{-3} ; wheat, 1.6×10^{-3} ; corn, 1.5×10^{-3} ; potatoes (tubers, per wet weight), 1.03×10^{-3} ; carrots (wet weight), 0.74×10^{-3} ; and tomatoes, 0.70×10^{-3} .

It was shown that the application of mineral fertilisers on sod-podzolic sandy loam soil for barley and oats in the recommended dose of $N_{80-100}P_{80-100}K_{80-100}$ pro-

vided a reduction in the content of ^{238}U in grain by 1.2–1.3 times. The high efficiency of mineral fertilisers in the reduction of the transfer of ^{238}U to barley and its accumulation in grain was noted at the fertilisation of the leached chernozem. This value came up to 1.4 times.

The accumulation of ^{238}U in the grain of oats and barley decreased by 1.5–1.8 times when the increased doses of phosphorus (P_{240}) and potassium (K_{240}) fertilisers were applied to sod-podzolic sandy loam soil. The application of lime in the background of $\text{N}_{80}\text{P}_{80}\text{K}_{80}$ provided a reduction of ^{238}U accumulation in the grain of oats and barley on sod-podzolic sandy loam soil by 2.1–2.6 times. The transfer of ^{238}U from soil to oats and barley decreased by 3.0–3.1 times during the application of humus.

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Factors Influencing the Soil to Plant Transfer of Uranium



Javier Guillén and F. M. Gómez-Polo

Abstract Uranium is a radioactive and toxic element present in the environment, but its concentration can be enhanced locally by human activities. An accurate knowledge of uranium transfer from soil to plants is essential to assure an adequate radiological protection, especially for crops consumed as foodstuff for men or cattle. Worldwide variation of transfer parameters is high, about 5–6 orders of magnitude, but usually lower than for anthropogenic radionuclides, such as Cs or Sr. There are some variables, reviewed in this chapter, that can influence this variation, as type of crop, part of plant considered, degree of association to soil particles, organic matter, and occurrence of chemicals, among others.

Keywords Uranium · Transfer · Speciation · Organic matter · Plant

1 Introduction

Uranium is a naturally occurring radionuclide that it is present in the environment. Uranium average concentration in soil ranges from 0.3 to 11.7 mg kg⁻¹ (UNSCEAR 1993), equivalent to a range of 3–117 Bq kg⁻¹ when considering ²³⁸U, the most abundant isotope. However, there are areas with higher uranium accumulation, which are usually mined for fuel in nuclear power plants. Other mining activities and industries also involve the occurrence of uranium in ores, by-products, or processed materials at higher concentrations. These activities are usually referred as NORM (natural occurring radioactive material) industries. Fertilizer production, coal-fired power plants, metallic mining, and gas and oil extractions are some of these NORM activities. Table 1 shows the range of uranium concentrations for various raw materials, by-products, and wastes from NORM industries, along with

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Table 1 Range of uranium concentration reported in several NORM industries

Fertilizer industry		
Product	U range (Bq kg^{-1})	References
Phosphate rocks	10–13,745	Guillén et al. (2014)
Phosphogypsum	<2–650	Guillén et al. (2014)
Fertilizer	62–7024	Guillén et al. (2014)
Scale	0.62–3510	IAEA (2003)
Mining industry		
Product	U range (Bq kg^{-1})	References
Coal	8.5–600	IAEA (2003); Xhixha et al. (2013)
Gold mine tailings	87.2–2668.9	Kamunda et al. (2016)
Tin mine tailing	1710–16,600	Ibeanu (2003); Ademola (2008)
Uranium mining		
Product	U range	References
Uranium mine tailing	400–41598 Bq kg^{-1}	Černe et al. (2010); Carvalho et al. (2006, 2007)
Drainage water	0.244–35.7 Bq L^{-1}	Carvalho et al. (2011)

those of uranium mining. As it can be seen, these activities can enhance uranium concentration up to several orders of magnitude above the usual range for soil.

Some of these products, such as different kinds of fertilizers, are specifically designed to be used in agriculture procedures in order to improve yield. Phosphate-based fertilizers (NPK, TSP, SSP, MAP, DAP) present a higher uranium concentration than the ones based on nitrogen, such as urea (Guillén et al. 2014). However, uranium concentration in plants grown using NPK fertilizer was reported to be similar to those grown without its use (IAEA 2003). This may reflect that the fertilizer doses used in soil were too low to be a radiological hazard. Other NORM by-products, such as phosphogypsum or fly ash from coal-fired power plants, can be also used as soil amendments (Papastefanou et al. 2006; Basu et al. 2009; Enamorado et al. 2014). Plants can also grow on mine tailings either from uranium or other metal mines. Uranium and other naturally occurring radionuclide concentrations in plant are usually enhanced compared to control sites outside the affected areas, and these differences can be applied for assessing the potential radiological hazard (Wichteray and Sawallisch 2002; Carvalho et al. 2009; Pourcelot et al. 2011).

2 Transfer Factors

The transfer processes from soil to plant can be modelled in different ways, in order to be properly quantified. The most usual approximation is the so-called transfer factors or concentration ratios, which are defined as the ratio between the radionuclide concentration in plant and in soil (Eq. 1):

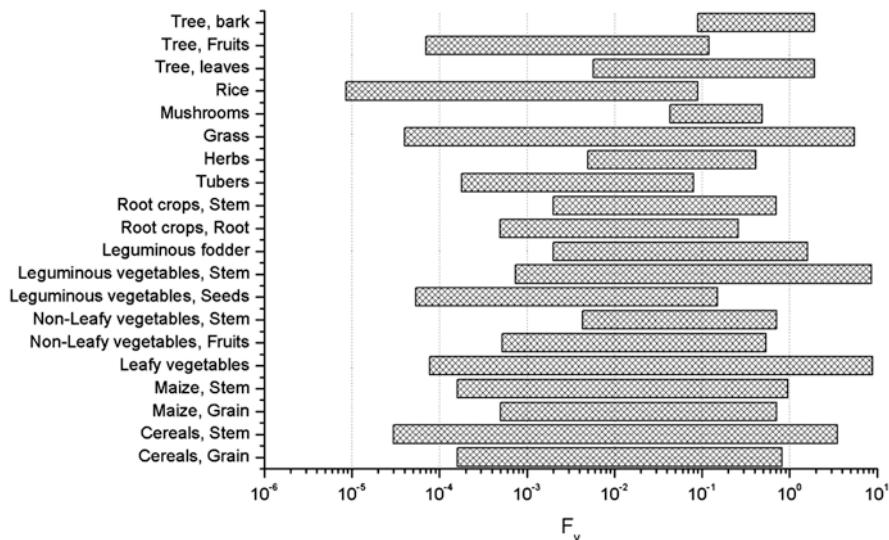


Fig. 1 Worldwide range of variation of transfer factor for uranium. Data from (Baeza and Guillén 2006; Blanco et al. 2010; Canha et al. 2010; Černe et al. 2010; IAEA 2010; Keser et al. 2011; Jeambrun et al. 2012; Lind et al. 2013; Štrok and Smodiš 2013; Sokolik et al. 2014; Kritsananuwat et al. 2015; Al-Hamarneh et al. 2016; Galhardi et al. 2017)

$$F_v = \frac{\text{Bq / kg d.w.plant}}{\text{Bq / kg d.w.soil}} \quad (1)$$

Depending on the part of plant considered, different transfer factors can be derived (Fig. 1). From the radioprotection point of view, edible plant parts, either for human consumption or intended for animal feeding, are relevant. Radionuclide concentrations in plants are usually expressed in dry mass, mainly to minimize differences in water content among species, but transfer factors based on fresh mass concentrations are also reported in the literature. Typical fresh–dry ratios for different plants species are available in IAEA TRS 472, Appendix I (IAEA 2010). The International Union of Radioecology (IUR) recommended a standardized root location in soil of 0–10 cm for grass and 0–20 cm for all other crops, including trees, assuming that all roots and all radionuclides present in the rooting zone are in that soil layer (IUR 1992). However, as uranium is naturally occurring, it is usually homogeneously distributed in soil, except for areas affected by uranium mines and NORM industries (IAEA 2003; Déjeant et al. 2014; Santos-Francés et al. 2018). The definition of transfer factor in Eq. (1) assumes a steady state in the ecosystem, so that radionuclide concentration in plants is proportional to that in soil. This steady state can be achieved upon the condition that radionuclide flow from soil to plants is negligible compared to the total amount in soil (IAEA 2010).

The transfer factor can be considered a first approximation to the problem. It assumes a quasi-equilibrium state in the environment so that transfer processes can

be considered as constant and linear. The validity of the linear approximation was questioned recently (Tuovinen et al. 2011, Tuovinen et al. 2016a,b). It was proposed that transfer processes may be approximated by Langmuir equation (Eq. 2):

$$C_{\text{plant}} = \frac{a \cdot b \cdot C_{\text{soil}}}{1 + b \cdot C_{\text{soil}}} \quad (2)$$

where C_{plant} and C_{soil} are the radionuclide concentrations in plant and soil, respectively, and a and b are fitting parameters. Usual transfer factors were reported not to be constant but decreasing with increasing soil concentration (Tuovinen et al. 2011). Therefore, the linear model may underestimate radionuclide concentration in plant for low soil concentrations. This nonlinearity was tested for several radionuclides in spruce needles (Tuovinen et al. 2016a) and a meso-cosmos (Tuovinen et al. 2016b). In the latter, the uranium uptake was nearly linear. One of the disadvantages of this model is that more information is required than compared to calculation of linear transfer factor values.

Figure 1 shows worldwide variation of uranium transfer factors for different plants/crops. A range about 5–6 orders of magnitude can be observed, which imply that soil to plant transfer of uranium is influenced by many variables. These variables can be biological (type of crop/plant, biological variability, nutritional requirements, etc.) and due to soil (pH, physicochemical composition, minerals present in soil, organic matter, nutrient availability, etc.). Compared with caesium and strontium transfer factors, uranium transfers values are 1–2 orders of magnitude lower (IAEA 2003). This can be attributed to the naturally occurring origin of uranium, as it is constituent part of some soil minerals.

Uranium is accumulated heterogeneously in different plant tissues. Uranium concentration distribution in whole plant in cereals is usually highest in roots, followed by stem and grain. Therefore, transfer values to roots are usually higher than to other plant tissues (Al-Hamarneh et al. 2016). Regarding trees, uranium accumulation decreased in the following order: root > leaves > stem > flower fruit (Blanco et al. 2010; Favas et al. 2016). High uranium root accumulation was also reported in greenhouse experiments with shoot/root ratio lower than 1, in the range 0.030–0.034 for sunflower (Alsabbagh and Abuqudaira 2017). Freshwater plants also present some differences between plant tissues, being root transfer parameters slightly lower than those for foliage or rhizome (Doering et al. 2018).

3 Factors Affecting the Uranium Soil-to-Plant Transfer

3.1 *Uranium Speciation in Soil*

As a consequence of the simple approach used in the definition of transfer factors (Eq. 1), chemical speciation of radionuclides is not considered. There are two main approaches for uranium speciation in soil: the use of sequential extraction procedures and the theoretical calculation of chemical species using

thermodynamic databases. The former approach assesses the degree of association/binding of radionuclides to soil particles based on successive application of reagents with increasing extraction/replacement power or designed to attack a specific geochemical phase. There is no unified sequential extraction procedure, and it is mainly defined operationally by different authors. However, there are some connections, as many sequential extraction procedures are based on that proposed by Tessier et al. (1979), which considered the following fractions in soil: (1) water soluble, extracted with double-distilled H₂O; (2) exchangeable fraction, extracted with 1 M ammonium acetate; (3) carbonated fraction, extracted with 1 M sodium acetate; (4) easily reducible fraction or bound to Fe and Mn oxides and hydroxides, extracted with 0.1 M hydroxylamine hydrochloride; (5) moderately reducible fraction, extracted with 0.2 M ammonium oxalate; (6) organic/hydrogen-sulfide fraction, extracted with H₂O₂ 30% and ammonium acetate; (7) acid fraction, extracted with HNO₃ 40%; and (8) residual fraction. This speciation scheme is widely used, especially for anthropogenic radionuclides in contaminated areas (Fawaris and Johanson 1995; Riise et al. 1990; Schultz et al. 1998; Rauret et al. 1999), and naturally occurring radionuclides in areas potentially affected by NORM industries (Blanco et al. 2004; Guillén et al. 2018; Pérez-Moreno et al. 2018). Other schemes are based on agricultural sequential extraction procedures based on the use of acids in several concentrations (Pavlotskaya 1974) and the extraction of organic matter (Cook et al. 1984). Due to the great number of speciation schemes, sometimes it is difficult to compare the results provided by two different procedures applied to the same soil (Blanco et al. 2004), given that they are not specific for a single geochemical fraction (Schultz et al. 1998). Other authors also compared different speciation schemes, reporting partial correlations between Tessier and Pavlotskaya methods (Guillén et al. 2018) or suggesting that Schultz method would perform better for uranium exchangeable fraction than Rauret method, acting as a better potential indicator to evaluate plant uptake in soils (Vandenhove et al. 2014). One of the major difficulties in assessing speciation schemes is the practically lack of certified reference materials, although some attempts of validation for naturally occurring radionuclides were carried out (Pérez-Moreno et al. 2018).

Bioavailable fraction is usually considered as the fraction of radionuclides that can be taken up or transferred to plants. Water-soluble and exchangeable fractions are usually considered as readily available for plants. Regarding exchangeable fraction, NH₄OAc is one of the most used reagents, although MgCl₂, CaCl₂, EDTA, DTPA, NH₄NO₃, KCl, or NaNO₃ might be used (Kennedy et al. 1997; Komosa 2002; Rigol et al. 2002). Other authors also considered reducible, oxidizable, and carbonated fractions to be mobile in soils (Rauret et al. 1999; Laurette et al. 2012a; Pérez-Moreno et al. 2018). As uranium is naturally occurring, it forms constituent part of minerals present in soil. Therefore, it is mainly associated with residual and other fractions strongly bounded to soil particles (Skipperud et al. 2013; Rout et al. 2015; Guillén et al. 2018). This association occurred in natural soils (Guillén et al. 2018) and in those affected by uranium tailings (Skipperud et al. 2013). However, if soils were artificially contaminated with uranium, it was mainly attached to exchangeable and carbonated fraction (Vandenhove et al. 2014).

The use of extractants with varying concentrations was reported to influence speciation results, increasing extraction/exchangeable capacity as concentration increased (Rout et al. 2015). Desorption capacity of CaCl_2 , MgCl_2 , and NaCl for uranium was reported to be proportional to ionic radius ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{2+}$) (Rout et al. 2015). Solid–liquid ratio in extraction procedure also had some influence, slightly increasing the amount of uranium extracted with increasing volume of NH_4OAc used until reaching saturation (Guillén et al. 2018). This effect depended on soil type.

Other nonconventional extraction procedures to assess uranium bioavailability were also reported in the literature for abandoned uranium mines, as the use of soft cola drinks (Lottermoser et al. 2011) or simulated physiological fluids (Foulkes et al. 2017). Lottermoser et al. (2011) compared uranium extracted with different types of cola soft drink, CaCl_2 , and DTPA (diethylenetriaminepentaacetic acid), obtaining similar results with classic cola and DTPA and reporting differences between different cola types. Foulkes et al. (2017) assessed the bioavailable fraction via simulated digestive fluids (saliva, bile, gastric, and duodenal fluids), reporting an amount between 3% and 7% of bioavailable uranium in waste solids and 5–36% in soils. This information is relevant when soil ingestion is considered, for instance, along with foodstuff.

Uranium chemical species present in soil and soil solution can be also theoretically estimated using thermodynamic and geochemical databases, such as J-Chess and PHREEQ (Laurette et al. 2012b; Mihálík et al. 2012; Hormann and Fischer 2013; Neiva et al. 2016; Boghi et al. 2018). These databases can be used to develop models for estimating K_d values (ratio between concentration in liquid and solid fractions) for different radionuclides. Regarding uranium, they consider exchange and complexation on clay silicate surfaces and complexation on hydrous ferric oxides and organic matter (Hormann and Fischer 2013; Boghi et al. 2018)

3.2 *Influence of Soil Properties*

The presence of ions in soil and soil solution can influence plant uranium uptake ability. Carbonate ions can increase uranium solubility via complexation reactions, occurring at pH 4 and higher, and also affect uranium sorption in ferric hydroxides (Li and Kaplan 2012; Boghi et al. 2018). On the contrary, complexation with phosphates reduces uranium bioavailability as insoluble uranyl phosphate is created (Laurette et al. 2012b). Uranium K_d values in soil increase with CO_2 pressure and are pH dependent, with maximum values in the range 5–7 (Hormann and Fischer 2013). Uranium concentration in soil can also be correlated with other metals, such as As, Fe, or Mn (Canha et al. 2010; Neiva et al. 2016), although this correlations should be considered as site dependent.

Organic matter in soil can also influence uranium uptake by plants. In organic matter-rich soils, correlation between uranium concentration in soil and percentage of total organic carbon was reported (Regensburg et al. 2010). Organic acid exudation

by roots can also modify uranium bioavailability. Complexation reaction with organic acids tends to increase uranium solubility in soil (Boghi et al. 2018). Citrate exudation can enhance uranium uptake and translocation from roots to shoots and leaves (Laurette et al. 2012b; Henner et al. 2018). Phytoremediation experiments also reported an increase in uranium concentration in plants and translocation from root to shoots (Mihalík et al. 2010, 2012), although not all plant species showed the same behavior. Transfer factor increased for root and leaves for willow; while for sunflower an increase for leaves and a decrease for roots were reported (Mihalík et al. 2010).

Uranium complexation with phosphates can reduce its concentration in plant tissues by precipitation and adsorption of uranium-rich clusters in epidermal cells (Laurette et al. 2012a, 2012b). Laboratory experiments showed the possibility of biomineralization of U(VI) phosphate as a result of microbial phosphatase activity but only with pure cultures (Beazley et al. 2011). Fungi can also precipitate uranium phosphate when growing on an organic source of phosphorus (Liang et al. 2015). Fungal phosphatase can hydrolyze organic phosphorus, releasing inorganic phosphate which can form uranyl complexes and later precipitate. Fungi present in soil can also enhance uranium uptake by plants, especially arbuscular mycorrhizal fungi associated with plants (Davies et al. 2015, 2018; Boghi et al. 2018). On the other hand, no correlation between uranium in roots and percentage of arbuscles, vesicles, or hyphae were reported (Davies et al. 2018).

4 Conclusion

The analysis of transfer processes in the environment, and especially involving plants, is essential to assure an adequate radiological protection of man and the environment. In this chapter, a review of the main factors influencing uranium transfer from soil to plant was carried out, showing that:

- The range of variation of transfer factors parameters for U and F_v presents a variation of 5–6 orders of magnitude worldwide and lower than those for Cs and Sr.
- U distribution is heterogeneous within plant, accumulating preferentially in roots.
- As U is naturally occurring, and therefore constituent of some minerals, it is mainly associated to residual or strongly bonded fraction in sequential extraction procedures.
- Soil amendments using citric acid enhance uranium uptake by plants, whereas when phosphate is added, U can become immobilized in soil.
- Organic matter in soil can enhance U uptake by plants, especially in those in symbiosis with arbuscular mycorrhizal fungi.

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Uranium and Plants: Elemental Translocation and Phytoremediation Approaches



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Abstract Uranium (U) is a ubiquitous element in nature, and ^{238}U is the most abundant radioactive isotope of uranium. Because of the use of U for military purposes in the past and increasing use of nuclear power during the last decades, U contamination in the environment, mainly as a consequence of mining, plays an increasing role. But also NORM (naturally occurring radioactive matter) industries release uranium and its progenies into the environment. Plants naturally incorporate U into their body via root uptake, where different factors play important roles and some plants are more efficient than others. This fact is made use of for plant-based remediation of contaminated sites. Selection of suitable plants that can uptake high amounts of the element without affecting their growth is very important. This review deals with uranium translocation in plants with a potential for phytoremediation practices.

Keywords Uranium · Uptake · Plants · Rhizosphere · Hyperaccumulator · AMF · Metal transporters · Radionuclide

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1 Introduction

Uranium is a lustrous, silvery-grey, dense (19 g cm^{-3}) metal of the actinide series. U has the atomic number 92 and atomic weight $238.02 \text{ g mol}^{-1}$. It is ubiquitously present in nature with an average concentration of less than 4 mg kg^{-1} (Nolan and Weber 2015; Tawussi et al. 2017) in rock, soil, water and all biosystems, including plants and humans. Three natural radioactive isotopes of U are common, with ^{238}U being the mostly abundant one (99.27%), followed by ^{235}U (0.72%) and ^{234}U (0.0054%). Radioactive isotopes of U have long half-lives (for ^{234}U , 244,000 years; ^{235}U , 710 million years; and ^{238}U , 4500 million years). They decay into various progenies, ultimately forming stable lead (Pb) (WHO 2012). Based on the fraction of ^{235}U , one classifies natural uranium (0.72% ^{235}U), enriched uranium (>0.72% ^{235}U) and depleted uranium (DU, <0.72% U). DU is used, e.g. in armour-piercing ammunition. There are several instances of DU release into the environment in the Gulf War, in former Yugoslavia and in Afghanistan, causing pollution of the environment and contamination of water and food sources (Pinney et al. 2003; Lloyd et al. 2009; Tasat et al. 2012). Mining of uranium caused (and still causes in less developed countries) severe contaminations of the environment. Since uranium coexists with many other substances, also mining of metals like the noble metals Au and Ag causes release of uranium to the environment through leaching and weathering of tailing material. The same is true for the NORM industries' oil, gas and coal exploitation but also use of geothermy. Furthermore, phosphate fertilizers contain considerable amounts of uranium, depending on their origin.

Overuse of groundwater is a concern of many countries worldwide. A recent study by Coyte et al. (2018) on groundwater quality in different states of India suggests considerably high prevalence of natural U, which exceeds the WHO (World Health Organization) provisional guideline value of $30 \mu\text{g L}^{-1}$ across India. Although, primarily, U is geogenic, though, huge water exploitation, decline of groundwater table and nitrate pollution typically augment the situation of U mobilization within the aquifers (Coyte et al. 2018). To avoid formidable situations related to U contamination and related human health risks, suitable remediation technologies must be adopted.

Apart from physical and chemical remediation practices, plant-based remediation is gaining its momentum due to its various advantages. Like any other elements, U translocation to a plants' body depends on its bioavailability. Several investigators working with plant-based U remediation practices (phytoremediation) suggested rhizofiltration as one of the important ways to decontaminate U from the contaminated environment (Dushenkov et al. 1997; Tomé et al. 2008; Baumann et al. 2014). Nevertheless, the process includes a number of soil factors, compositions, bioavailability/mobility (Gupta and Walther 2014) and also availability of the U, chelating agents, robust sorption and precipitation activities by the plants (Lee and Yang 2010). Addition of chelating substances in soil can alter the U availability to the plant, but also increase the U concentration in the ambience, which may lead to reduction in plant growth and phytoremediation efficiency (Lozano et al. 2011;

Baumann et al. 2014). Chelating agents and other chemicals are efficient, selective scavenger and also play an important role in U/DU accumulation, which decrease the absorption and distribution and increase the elimination of U (Yue et al. 2018). A number of plants, like *Lemna gibba* (duckweed), *Callitriches stagnalis* (water-starworts), *Fontinalis antipyretica* and *Apium nodiflorum*, are reported to have potential for U remediation (Mkandawire et al. 2004; Pratas et al. 2012; Favas and Pratas 2013). *C. stagnalis* and *A. nodiflorum* are regarded as keystone species for phytoremediation applications of U for their efficient rooting capabilities and bio-productivity (Favas and Pratas 2013). Further, soil mycorrhiza (including AMF, arbuscular mycorrhizal fungi) plays a considerable role in phytostabilization of U (Chen et al. 2008; Gadd and Fomina 2011). Conversely, plant stress and related ROS (reactive oxygen species) production for radionuclide accumulation are also evident from different studies (Gupta and Voronina 2018) which are important for appropriate plant-based remediation practices of uranium.

2 Uranium and Its Application

Uranium has a major application in nuclear power reactors as fuel, while depleted U is generally used to make military components, but also (formerly) used in paint and pigment manufacturing units (Berlin and Rudell 1986; WHO 2012). Electricity production by low-carbon electricity in nuclear power plants increased worldwide during the last few decades. Currently, nuclear power provides approximately 11% of global supply of electricity and is expected to rise as it is seen by many countries as a cost-competitive, near-zero pollutant (including greenhouse gases)-emitting technology, with a scope for industrialized nation having limited resources of native resources (WNA 2017). For example, France relies on nuclear for more than 75% of electricity and the USA, about 20%. Nevertheless, evolution of nuclear power facilities and related U requirement is undergoing uncertainties worldwide after the accident in Fukushima (Japan) in March 2011 (NEA 2016). Countries like Kazakhstan, Canada and Australia produce around 39, 22 and 10% of U, respectively, which amount to more than two-thirds of the global U production (59,531 tonnes from mines) (WNA 2017). The production of U may come from in situ leaching (ISL; 50%), underground and open pit (46%) or by-products (4%). Apart from natural leaching, U enters into the environment from nuclear fuel plants and their tailings, phosphate fertilizers, coal and fuel combustion, etc.

3 Uranium in the Environment

In spite of its ubiquitous presence in the environment, U has peculiar chemical and physical properties. Radiologically, U is an alpha-particle-emitting, chemically toxic, non-essential element. Apart from the readily soluble hexavalent form,

uranium may be present as U(IV)-oxide. Due to the very low solubility of U(IV) in environmental media, it often is present in particulate form (diameter of 0.1 microns or less) which may confer higher biological toxicity (Tasat et al. 2012). Being reactive in nature, U persistently binds to nucleotides and proteins and affects citrate, lactate, carbonate, pyruvate and phosphate metabolisms after entering in the body primarily through inhalation, but also by dermal contact and ingestion (Tasat et al. 2012).

U(VI) is mobile in soil, which exists in solution UO_2^{2+} and as soluble carbonate complexes, like $\text{UO}_2\text{CO}_3^{\circ}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})^{3-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and plausibly $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ (Grenthe et al. 1992; Duff and Amrhein 1996). Meinrath et al. (1996) suggested that U(VI) primarily exits in hydrolysed forms in pH 4.0–7.5, while vented air may affect clay lattice of the soils creating less transferrable and solvable forms of U, leading to limited availability to plants (Bunzl et al. 1995; ANRCP 1998). Sheppard and Thibault (1992) showed that Fe-Mn oxide association is common in U(VI) spiked soil, where rate of desorption of the element increased with time.

4 Plant-Based Remediation

Appropriate eco-friendly U remediation technologies for U-contaminated soil and water are an important research area. Apart from physical and chemical methods, application of bioremediation, including phytoremediation technology, is useful for decontamination of U contamination from the environment.

Remediation of organic and inorganic molecules using plant species to achieve site-specific cleaning is the basis of phytoremediation (Ancient Greek: phyto—‘plant’ and Latin remedium—‘restoring balance’). This technique is environmentally friendly and cheap in comparison to the conventional instrument and/or chemical-based environmental restoration processes. Microbial diversity at rhizosphere and plant and its exudates along with soil properties are essential factors for elemental uptake and accumulation (Gupta et al. 2016a). After the Chernobyl accident in 1986 (UNSCEAR 2010) that caused huge release of radionuclides into the environment, scientists thought for phytoremediation of contaminated sites. In 1998, PhytoTech, Consolidated Growers and Processors (CGP) and Institute of Bast Crops (Ukraine) came up with plant industrial hemp (cannabis) for phytoremediation. The process was further developed by USEPA and US Department of Defense extensive clean-up projects to eliminate toxins and specific metals (Rai and Pal 1999; Gupta et al. 2016a). The elements including toxic cations or oxyanions are extracted from the soil and are translocated into the above-ground parts of plants forming less toxic substances (Chatterjee et al. 2012). Processes like exclusion, stabilization, detoxification and partitioning (storing in particular tissues and cell organelles like cell walls, vacuoles) to a particular metal are strategically characteristics to a plant, which may also develop antistress responses through proteins like phytochelatins and metallothioneins. In phytoremediation practices, these processes

are termed as phytostabilization, rhizofiltration, phytoextraction, phytovolatilization, phytostimulation and phytodegradation (Greipsson 2011; Chatterjee et al. 2013; Gupta et al. 2016a). Suitable candidate plants for phytoremediation are plants that are capable of uptaking elements from soil in remarkably huge quantities (like 100–1000-fold higher concentrations than their normal counterparts), without showing any indications of phytotoxicity (Reeves 2006). Plants of families like Asteraceae, Araceae, Papilionaceae, Brassicaceae, Poaceae and Caryophyllaceae are reported to be best candidate for phytoremediation (Gupta 2013). Tang and Willey (2003) reported that plants from Araceae family (e.g. *Lemna minor*, *L. gibba*) can render higher bio-removal capacity for radionuclides including U. Therefore, phytoremediation can be used for affordable long-term treatment to remediate radionuclide-contaminated areas (Gupta and Walther 2014; Gupta et al. 2016a).

5 Membrane Transport and Rhizosphere for Uranium Phytoremediation

A variety of metal transporter proteins present in the plasma membranes of root cell play significant roles in elemental transport and homeostasis. These transporters which belong to families like zinc importer (ZIP) families (ZRT, IRT-like protein [ZRT, zinc-regulated transporter, IRT, iron-regulated transporter]), natural resistance-associated macrophage protein (NRAMP), cation diffusion facilitator (CDF) family, copper transporter (COPT) heavy metal ATPase (HMA) family like P1B-ATPases, ATP-binding cassette (ABC) transporters, ABC transporters of the mitochondria (ATM), Ca^{2+} cation antiporter (CAX), multidrug resistance-associated proteins (MRP) and yellow-stripe-like (YSL) pleiotropic drug resistance (PDR) transporters are well-studied transporters (Dubey 2011; Huang et al. 2012; Gupta et al. 2013, 2016a). Cd transport from root to shoot, as, for example, in *Arabidopsis thaliana*, occurs through AtZIP4 (ZIP4) proteins (Krämer et al. 2007). Proton pumps like vacuolar proton pyrophosphatase (V-PPase) and vacuolar proton-ATPase (V-ATPase) are important transporters for vacuolar sequestration (Dalcroso et al. 2010; Manara 2012).

Plant roots secrete a number of components (exudates) at the rhizosphere (soil–root interface) that help to increase immensely the richness of bacterial and fungal communities of soil (Anderson et al. 1994). Root exudates include excretions (e.g. protons, bicarbonates, carbon dioxide, etc.), diffusates (e.g. organic acids, amino acids, water, sugars, inorganic ions, etc.) and secretions (e.g. siderophores, mucilage, allelopathic compounds, etc.) that modify composition of soil microflora community having unique gene pool for improved metabolic capabilities (Hall 2002; LeDuc and Terry 2005; Gupta et al. 2016a). For example, ammonium nitrate and citric acid augmentation helps plants to have increased availability of uranium. However, Prasad (2011) pointed out the risk of augmenting soil, which must be done in an appropriately managed manner. Plant growth-promoting rhizobacteria

(PGPR) perform vital role by increasing the production of growth regulators (e.g. gibberellic acid, indole acetic acid, cytokinins and ethylene). Rhizobacteria also produce phosphate-solubilizing agents, antibiotics, hydrocyanic acid, siderophores, etc. that escalate metal bioavailability and root absorption (Davies Jr et al. 2001; Gupta et al. 2016a).

6 Uranium Uptake by Plants

Uptake of several essential elements from soil is a natural phenomenon in plants (Fig. 1). However, during the process of uptake, non-essential analogous elements that are present in the environment enter into the plant's body by comparable mechanisms. Some factors including agroclimatic conditions, soil properties, pH, mineral and organic constituents, soil microbial communities, chelating agents, etc. influence the uptake process and accumulation of any element (Walther and Gupta 2015). Nevertheless, decontamination of polluted environment using plants is of great interest in recent time (Gupta et al. 2016a). Behaviour of U in soil is an important factor for understanding phytoremediation of this element as is having different chemical species, which are of diverse solubility and biological accessibility patterns (Mitchell et al. 2013; Newsome et al. 2014). For example, in oxic milieus, hexavalent U(VI) usually occurs in the hydrated state (UO_2^{2+} soluble uranyl ion, schoepite, etc.), while less soluble compounds are formed in anoxic environments (Ebbs et al. 1998; Boghi et al. 2018). Although soil organic matters like clay mineral particles adsorb UO_2^{2+} , solubility increases if specific ligands like carbonates are present in solution (Davis et al. 2004; Bryan et al. 2012; Cumberland et al. 2016). Regulation methods of U uptake and translocation by plants are not clearly understood. Effective phytoremediation for ameliorating U-contaminated soil depends upon various factors like solubilization, absorption, transportation and accumulation within plants. It was observed that low pH enhances the root-to-shoot uptake and translocation of U, which varies amongst species (Saenen et al. 2015; Favas et al. 2016). But large accumulation of U within shoot is toxic for plants creating oxidative stress (Saenen et al. 2015). Mycorrhizal fungi play an important role in U uptake and translocation. Due to solubilization by mycorrhizal fungi at rhizosphere, although plant uptake of U increases, though, impediments of root-to-shoot translocation have also been reported (De Boulois et al. 2008; Davies et al. 2015; Boghi et al. 2018). Gupta et al. (2016b) working with hydroponically grown *Pisum sativum* plant reported that H_2O_2 production was higher in experimental concentration of $[\text{U}] = 25$ and $50 \mu\text{M}$, with higher U accumulation in roots than shoots. However, damage to the membranes of both root and leaves was recorded due to the accumulation of U signifying oxidative stress and related toxic mechanisms (Gupta et al. 2016b).

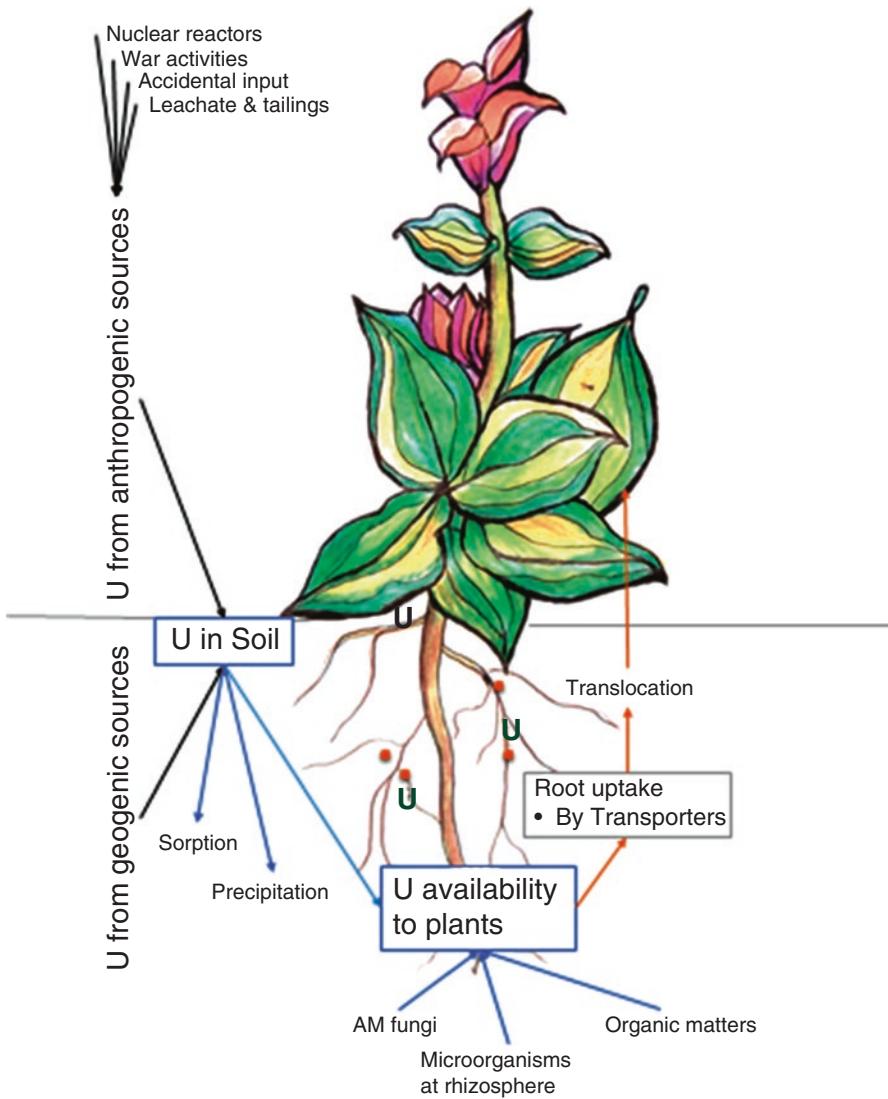


Fig. 1 Schematic representation of uranium uptake and translocation in plants. Uranium enters into the soil both from anthropogenic and natural (geogenic) sources. Availability of uranium to plants depends upon several soilborne factors and plants species for transporting from soil to plants parts (U, uranium)

7 Microbial Activities on Uranium

Adsorption of U compounds onto the bacterial cell surface is a natural phenomenon, as it provides an efficient matrix for complexation of the element at low pH conditions; however, Acharya et al. (2009) pointed out that *Synechococcus elongatus*, a marine cyanobacterium, has the capacity to bind of uranyl carbonate even at pH 7.8. Sequestration of U is also observed in *Anabaena torulosa*, a marine, nitrogen-fixing cyanobacterium, which can be removed from the bacteria through acidification (Acharya et al. 2012; Acharya and Apte 2013). In general, bacterial cells provide high surface to volume ratio and represent a number of polymers (like lipopolysaccharides, peptidoglycan, glycolipids and proteins) on their cell surface that act as metal-binding ligands (Beazley et al. 2007; Acharya 2015). Bacteria show various adaptive strategies to survive in the U mining fields. Working on U-tolerant soil bacteria of Domiasiat deposit of U ore in Northeast India, scientists have pointed out that phosphatase-positive phenotype was dominant (around 76%) with *Firmicutes* (51%) and *Gammaproteobacteria* (26%) and is most dominant with considerable amount of *Actinobacteria* (11%), *Bacteroidetes* (10%) and *Betaproteobacteria* (2%) (Kumar et al. 2013a, b; Acharya 2015). *Serratia marcescens* and *Burkholderia arboris* are reported as potential species for U precipitation and decontamination (Acharya 2015).

8 Accumulation of Uranium in Plants

Accumulation of U varies in different plant species. Researchers have cited various toxic effects in different plant species. In tomato plants, Gulati et al. (1980) reported a decrease in yield in soil U level from 1 to 6 mg kg⁻¹. Sheppard et al. (1992) reported higher biomass having soil U levels of 10,000 mg kg⁻¹ in *Brassica rapa*, while other plants showed harmful effects above 300 mg kg⁻¹ U in soil. Entry et al. (1996) reported higher accumulation (5000–10000 times higher) of U in sunflower from contaminated aquatic ambience. Studying on phytoremediation with plant *Brassica juncea* in organic-amended soil, researchers reported that accumulation of U in shoot increased from 5 mg kg⁻¹ to more than 5000 mg kg⁻¹ (Huang et al. 1998; ANRCP 1998). Dushenkov et al. (1997) reported that sunflower plants were having potential to treat U-contaminated water, streams through the process of rhizofiltration, where bioaccumulation coefficients of U concentrations (roots: aqueous phase) reached 30,000. Shtangeeva et al. (2006), working with natural plant species wheatgrass (*Triticum repens* L.) and plantain (*Plantago major*) on U and Th (thorium) uptake after soil application, revealed that uptake was more efficient for U than for Th. Further, it was observed in the study that soil microbiota at rhizosphere changed significantly and chlorophyll content of the plants decreased (Shtangeeva et al. 2006). Stojanović et al. (2012) reported that *Nicotiana tabacum* L. (tobacco plant with Virginia and Burley varieties) is a potential hyperaccumulator plant for U

phytoremediation, leaves of which can accumulate higher amounts of U when they were grown on uranium mine tailings. Amending soil with bioagents like AMF (arbuscular mycorrhizal fungi) and chemicals like phosphate, calcium carbonate, citric acid, etc. can augment phytoremediation by increasing the bioavailability of U (Malaviya and Singh 2012). Mycorrhizae are abundant in nature forming root-fungus associations. Three types of mycorrhizae are common, namely, arbuscular mycorrhizae (AM, formed mainly by herbaceous plants), ectomycorrhizae (ECM, formed mainly by forest trees) and ericoid mycorrhizas (of plants like the Ericaceae). Association with arbuscular mycorrhizae provides several benefits to the plant, including growth, disease resistance, better crop quality, survival and tolerance to troubled sites. Mycorrhizal association with plant roots modulates functioning of the plants to grow in distressed sites contaminated with heavy metals like U (Shaker-Koohi 2014). Rufyikiri et al. (2002), working on AMF *Glomus intraradices* with bacteria *Agrobacterium rhizogenes*, transformed carrot (*Daucus carota*) for U uptake and translocation and found that U hyphae number influenced the U translocation in plant root. In another study with essential ³³P and non-essential ²³³U with carrot introduced with AMF (*G. intraradices*), Rufyikiri et al. (2004) demonstrated that translocation of ³³P is much higher than ²³³U, suggesting AMF's efficient segregation mechanisms for non-essential elements such as uranium. Charro and Moyano (2017), working with ²³⁸U, ²³²Th, ²²⁶Ra, ²²⁴Ra and ²¹⁰Pb uptake in trees like *Quercus pyrenaica* and *Quercus ilex rotundifolia* of dehesa ecosystem, found that there was no influence over the transfer factors and radionuclide contents, but concentration of the metal may affect.

9 Conclusive Remarks

Phytoremediation is a promising technology for restoration of sites contaminated by radionuclides (in particular uranium) or other toxic metals. Chemistry- and engineering-based remediation processes have a number of apprehensions for their higher energy and economic implications. Yet, effective application of plants depends upon factors like the plant's ability to uptake the element in relatively high concentrations without affecting their growth and biomass production. Other edaphic factors like soil and clay properties, presence of other minerals and organic matters and availability of the desired elements to the plants are important. Amendments of soil with organic acids like citric acids have shown considerable difference in remediation practices by transiently reducing the pH of soil that improves desorption of soil U. Several plants like *C. stagnalis*, *F. antipyretica*, *A. nodiflorum* and *B. juncea* are having the potential for U remediation. Along with cultivar selection, genetic manipulation of metal transporters, elucidating factors related to growth and antistress are important areas of research which will help to apply phytoremediation more decisively. Therefore, comprehensive multidisciplinary research on contamination factors, AMF and associated rhizosphere related

to plant-based remediation may prove beneficial to decontaminate environment of contemporary nuclear age.

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Soil-to-Crop Transfer Factor: Consideration on Excess Uranium from Phosphate Fertilizer



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Abstract In this chapter, we used the initial U/Th concentration ratio in nonagricultural soil samples to estimate the concentrations of excess U ($_{\text{ess}}\text{U}$) in agricultural fields in Japan due to long-term application of phosphate fertilizers as a means to understand the bioavailability of added U to soil. We carried out a data survey and obtained initial U/Th ratios from 210 nonagricultural soil samples collected throughout Japan; the values are distributed log-normally, and they ranged from 0.006 to 0.9 with the geometric mean value of 0.259. Because concentrations of Th are lower in phosphate fertilizers than those of U, we assumed that Th concentrations in agricultural fields kept their initial values. Thus, the geometric mean of initial U/Th and Th concentration in each agricultural soil sample was used first to calculate the initial U concentration in the soil sample, and then, by subtracting the value from total U in the soil sample, the $_{\text{ess}}\text{U}$ concentration in the soil was estimated. Uranium in phosphate fertilizer was thought to be soluble so we hypothesized that $_{\text{ess}}\text{U}$ would be easily taken up by crops; however, there were no correlations between brown rice and $_{\text{ess}}\text{U}$ nor for potato and $_{\text{ess}}\text{U}$. These results suggested that the added U was fixed to the soil particles so that $_{\text{ess}}\text{U}$ would not be easily taken up by crops. We also found that there was no significant difference between soil-to-crop transfer factors obtained in low and high $_{\text{ess}}\text{U}$ soil conditions for brown rice and potato; this means that the $_{\text{ess}}\text{U}$ and the initial U in soil-to-crop systems had the same fate. Thus, soil-to-crop transfer factors obtained using U in agricultural fields should be valid in long-term radiation dose assessment models.

Keywords Environmental dose assessment · Phosphate fertilizer · Soil-to-crop transfer factor · U/Th concentration ratio · Rock · Soil

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1 Introduction

Carbon dioxide is one of the major causes of global warming; therefore, demands are increasing for electricity generation technologies which emit less CO₂ than power plants using fossil fuels. One of the possible technologies is to use nuclear power plants which employ nuclear fuel. After the nuclear fuel has been burned for about 3 years, the spent fuel is removed from the reactor and stored to allow short-lived radionuclides to decay and lower the amounts of spent fuel radioactive wastes that must be disposed of and managed long-term. There are two options for the spent fuel: direct disposal to deep underground with long-term management or recycling to extract uranium (U) and plutonium for further use by separating them from the high-level radioactive wastes that must be also disposed of and managed long-term. In both cases, nuclear wastes containing different levels of U are going to be disposed into deep underground. For the long-term environmental safety assessment of the radioactive waste disposal sites, mathematical models have been used. Among the environmental transfer parameters used in these models, soil-to-crop transfer factor (TF), which is defined as the ratio of a radionuclide concentration in crop to that in soil, is a key parameter that directly affects the internal dose to humans through the ingestion pathway.

To obtain the TF of U, we might be able to use naturally existing U to predict the behavior from radioactive waste disposal sites to the biosphere. However, the physicochemical forms of the initial U in soil and added U would not be the same. Vandenhove et al. (2014) carried out sequential extraction to identify the physicochemical forms of U in soils. One of their samples was collected from the Namur region, Belgium, which has a high natural background level of U, and the other five samples were contaminated with U from different sources; therefore, they used one sample containing U initially included in the soil (taken from the high natural background level area) and artificially U added soil samples. Their results showed that the U distribution fractions differed among the studied soil samples; for example, ca. 30–50% of U initially included in the Namur soil are distributed in acid soluble+residual fractions, but soil samples contaminated with UO₂(NO₃)₂·6H₂O had less U distributed in these fractions (ca. 4–5% of total U). Interestingly, Vandenhove et al. (2014) found that soil samples contaminated by the waste stream from a phosphate industry facility showed similar results to those observed for the Namur soil. It should be mentioned that U behavior in soil is affected by not only the chemical forms of added or initial U but also the soil characteristics; therefore, it is difficult to conclude that the physicochemical forms of initially included and added U were significantly different. Another example was presented by Yamaguchi et al. (2009); they used samples from four agricultural fields for which both non-fertilizer added soil and long-term phosphate fertilizer added soil were available from each field. It has been reported that phosphate fertilizer contains a high amount of U and soil to which phosphate fertilizer has been applied has more U than soil has not had the fertilizer application (Komura et al. 1985; Tsumura and Yamasaki 1993; Pantelica et al. 1997; Yamazaki and Geraldo 2003). Thus, an excess amount of U

($_{\text{ess}}\text{U}$) should be found in agricultural fields due to the phosphate fertilizer application (Rothbaum et al. 1979; Jones 1992; Tagami and Uchida 2006; Takeda et al. 2006; Yamaguchi et al. 2009). When Yamaguchi et al. (2009) applied chemical extraction methods to identify constituents that contributed to U fixation in the studied soil samples, they observed that the physicochemical forms of U initially included and added were different. According to their results, most of the U from the phosphate fertilizer was incorporated into the soil organic matter and amorphous Fe/Al oxy-hydroxides in the soil, which meant the $_{\text{ess}}\text{U}$ was not readily available to crops; but it was not clear whether the $_{\text{ess}}\text{U}$ in soil correlated with the U concentrations in crops or not.

If the concentrations of $_{\text{ess}}\text{U}$ in agricultural soils were estimated and then the concentrations between $_{\text{ess}}\text{U}$ in soil and U in crops were compared, it might be possible to determine whether or not the soil-to-crop transfer of added U, that is $_{\text{ess}}\text{U}$, would affect the U concentrations in crops. If $_{\text{ess}}\text{U}$ in soils and U in crops were well correlated, $_{\text{ess}}\text{U}$ might have different soil-to-crop transfer factors compared to those that initially included U have. Such results would make it difficult to apply TF values obtained by measuring total U in soil and crops to the mathematical models needed for dose assessment from radioactive waste disposal sites. In this chapter, therefore, we try to estimate $_{\text{ess}}\text{U}$ in agricultural field soil, that is, paddy field and upland field, using the initial U/Th ratio in soil because the Th concentration in phosphate fertilizer is generally low (Komura et al. 1985; Tsumura and Yamasaki 1993; Pantelica et al. 1997). Thus, Th in agricultural fields would not increase much even if phosphate fertilizer was applied in those fields, which would allow us to calculate the initial U from the Th. After examining the effect of estimated $_{\text{ess}}\text{U}$ to the U contents in crops, we provided the TF-U values for ten crop groups collected from studies done in Japan.

2 Estimation of Excess Amount of U in Agricultural Fields

According to Th and U concentration data obtained for about 3000 Japanese river sediment samples by Imai et al. (2004), a good correlation factor between Th and U concentrations was found (Fig. 1), i.e., $R = 0.859$ ($p < 0.001$), between logarithms of the concentrations of Th and U (log-normal curves fit the data better than normal curves, so that logarithms of the data were used). However, for agricultural fields, we previously reported no correlation between Th and U concentrations for 37 paddy field soil samples and a correlation factor of $R = 0.69$ ($p < 0.001$) for 45 upland field soil samples which is lower than that of the river sediment samples (Tagami and Uchida 2006). Although we increased the sample numbers in this study, i.e., $N = 98$ for paddy soil samples and $N = 139$ for upland soil samples collected throughout Japan, the correlation factor for each soil use was still low, i.e., $R = 0.472$ ($p < 0.001$) for paddy field soil samples and $R = 0.659$ ($p < 0.001$) for upland field soil samples (Fig. 2). Apparently, application of phosphate fertilizers to agricultural fields affected these observation results.

Fig. 1 Correlation between concentrations of U and Th in river sediment samples (data adopted from Imai et al. 2004)

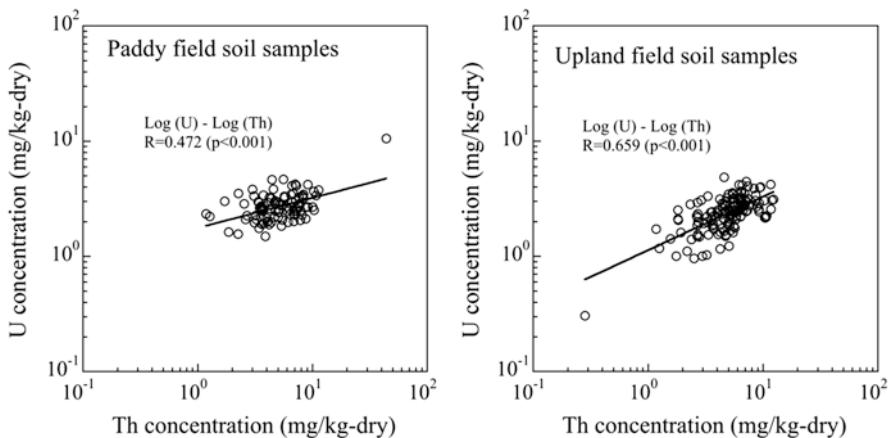
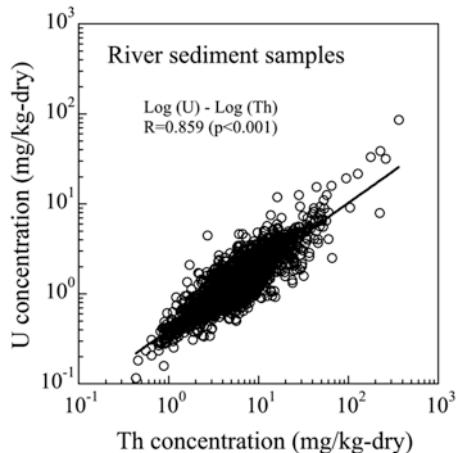


Fig. 2 Correlations between concentrations of U and Th in paddy field and upland field soil samples collected in Japan

To estimate the $_{\text{ess}}\text{U}$ concentration in a soil sample, $[_{\text{ess}}\text{U}]$, we used the following equation:

$$[_{\text{ess}}\text{U}] = [t - \text{U}] - [t - \text{Th}] \times _{\text{init}} \text{U} / \text{Th} \quad (1)$$

where $[t - \text{U}]$ and $[t - \text{Th}]$ are total concentrations of U and Th in the agricultural soil sample and $_{\text{init}}\text{U}/\text{Th}$ is the initial U/Th ratio calculated from U and Th concentrations in nonagricultural field soil samples. Takeda et al. (2006) applied $_{\text{init}}\text{U}/\text{Th} = 0.28$ because that was the value found in deeper layers of their observation field. Unfortunately, however, we cannot supply a suitable $_{\text{init}}\text{U}/\text{Th}$ for each soil sample using a similar method to that of Takeda et al. (2006); therefore, a typical value was derived for this study (see Sect. 2.1).

2.1 Correlations Between Th and U Concentrations in Nonagricultural Soil Samples

Previously, we used $_{\text{init}}\text{U}/\text{Th} = 0.23$ (Tagami and Uchida 2006) based on some non-agricultural soil U/Th ratios; we did a further data survey to get a more reliable $_{\text{init}}\text{U}/\text{Th}$ ratio in soil (nonphosphate fertilizer affected). For this purpose, it is better to use nonagricultural soil data. We selected ^{232}Th and ^{238}U activity concentrations in non-agricultural soil samples from Environmental Radiation Database (NRA 2018) if these two radionuclides were measured in the same soil sample collected at the same sampling time. We converted the database values of radioactivity concentrations ($\text{Bq kg}^{-1}\text{-dry}$) into mass concentrations ($\text{mg kg}^{-1}\text{-dry}$) by multiplying Th activity concentrations by 0.246 mg Bq^{-1} and U activity concentrations by $0.0804 \text{ mg Bq}^{-1}$ before finally calculating $^{154}\text{U}/\text{Th}$ concentration ratios.

A further literature survey allowed us to add more U and Th concentration data from 54 samples (Mizohata et al. 1977; Terashima et al. 2004; Kano et al. 2009; Sahoo et al. 2011, 2013) and one U/Th ratio (Takeda et al. 2006). In total, 210 samples with U/Th data for nonagricultural soil samples from 21 out of 47 prefectures in Japan were collected. The correlation of U and Th concentrations in the collected nonagricultural soil samples is plotted in Fig. 3. We found a high correlation factor of $R = 0.873$ ($p < 0.001$) just as found for river sediment samples. Thus, generally, Th and U should be correlated well in soil, but in agricultural fields, they were not.

The obtained U/Th data are summarized in Table 1. The data is distributed log-normally (Fig. 4), and the distribution was narrow; therefore, the geometric mean (GM) value of the U/Th ratio was calculated. Yamagata and Iwashima (1967) and Minato (2005) also reported Th and U concentrations in nonagricultural soil samples in Japan so that their results are listed in the same table, too. For the data by Yamagata and Iwashima (1967) and Minato (2005), we simply calculated the GM

Fig. 3 Correlation between concentrations of U and Th in nonagricultural soils

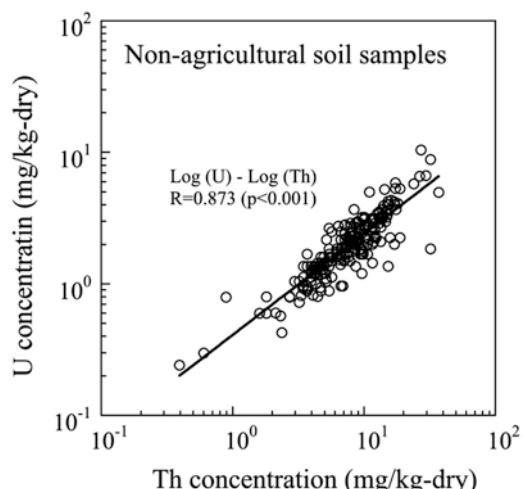
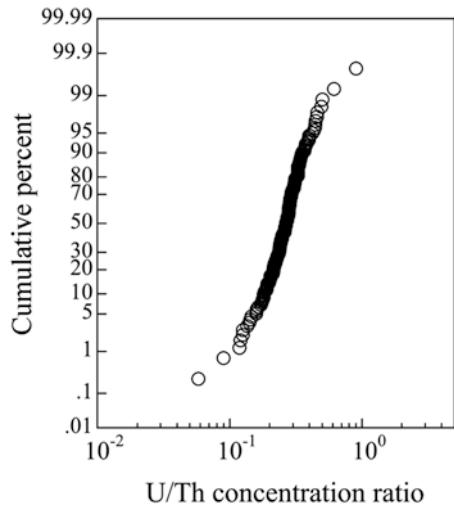


Table 1 Uranium and thorium concentrations and geometric mean (GM) U/Th ratio in nonagricultural soils and river sediments collected in Japan

Data source	Th mg kg ⁻¹ -dry	U mg kg ⁻¹ -dry	U/Th ratio (range)	Comments
Nonagricultural soils, This study	7.35 (0.39–36.9)	1.90 (0.24–10.5)	0.258 (0.058–0.899)	210 samples, 21 prefectures
Nonagricultural soils, Minato (2005)	8.13 (3.88–29.4)	1.84 (0.97–5.96)	0.237 (0.179–0.306)	Data summarized for 15 samples (from 1308 samples), 8 prefectures
Nonagricultural soils, Yamagata and Iwashima (1967)	5.44 (3.0–9.3)	1.19 (0.26–2.89)	0.219 (0.048–0.567)	Data for 22 composite samples (prepared from 172 samples), all Japan
River sediments, Imai et al. (2004)	5.45 (0.43–363)	1.32 (0.12–86.2)	0.241 (0.036–1.65)	3024 samples, all Japan

Fig. 4 Distribution of U/Th ratio in nonagricultural soil samples calculated in this study



values of their reported values. Yamagata and Iwashima (1967) collected 172 samples throughout Japan from which they made 22 composite samples that had the GM = 0.219 by our calculation. Minato (2005) surveyed literature values, and he had 1308 data sets (data were summarized into 15 groups) from eight prefectures that had the GM = 0.237 by our calculation. Although our sample numbers were smaller than those reported by Minato (2005), our area coverage was larger, and we could obtain more data than those reported by Yamagata and Iwashima (1967); therefore, we decided to use our own U/Th data including data from Yamagata and Iwashima (1967) and Minato (2005). The GM value of our U/Th data was 0.258, and the value was used hereafter in this study as “_{init}U/Th.”

Although we decided to use a single value for $_{\text{init}}\text{U}/\text{Th}$ ratio in this study, additional information on the U/Th ratios in nonagricultural soils was provided by comparing to those of their bedrock data. Table 2 summarizes U/Th data in some Japanese bedrock (Tezuka 1972; Ebihara et al. 1984; Katoh et al. 1985; Shibata and Nakamura 1997; Kimura et al. 2003) including rock reference materials prepared by the National Institute of Advanced Industrial Science and Technology (AIST 2018). In geochemistry, use of fractionation of U from Th in rocks has been applied successfully to understand the geological conditions of the rocks. The U/Th concentration ratios differ by types of rock due to their generation and aging processes; volcanic and plutonic bedrocks ranged from 0.15 to 0.51, and sedimentary bedrocks showed a large variation from 0.25 to 61. As Takeda et al. (2006) reported, it was clear that the U/Th concentration ratio in a soil reflected that in its bedrock; therefore, to have a more precise $_{\text{ess}}\text{U}$ datum in an agricultural soil, $_{\text{init}}\text{U}/\text{Th}$ datum in its bedrock is necessary, but collecting such datum is usually impossible. In the same table, we list U/Th values for soils that had known bedrock types (Minato 2005). Because U is slightly more mobile than Th is (e.g., Tomé et al. 2002), the U/Th values tended to be smaller in nonagricultural field soils than that in bedrocks.

2.2 Concentrations of Estimated $_{\text{ess}}\text{U}$ in Agricultural Fields

Agricultural soil samples were collected throughout Japan; in agricultural fields, total U concentrations were from 1.5 to 10.6 mg kg⁻¹-dry for 98 paddy field soil samples and 0.31 to 4.9 mg kg⁻¹-dry for 139 upland field soil samples. These data were measured by ICP-MS after dissolving the powdered soil samples using mineral acid in a microwave oven. Details of the method were reported elsewhere (Uchida et al. 2007a). Total U concentrations in both uses are distributed log-normally (Fig. 5); therefore, logarithms of the data were used to compare concentrations among different uses. The results showed that total U concentrations were higher in paddy fields than in upland fields by *t*-test ($p < 0.01$). For upland fields, the soils are generally oxic; therefore, U(VI) is the dominant chemical state and it is relatively mobile in the soil. However, in paddy fields, because the soils are under reducing conditions during rice planting, U would exist in the forms of insoluble U(IV) minerals. Once U(IV) is generated in soil, its insoluble forms can be remobilized due to formation of carbonates from microbial respiration (Wan et al. 2005; Zhou and Gu 2005). Therefore, the U fates in soil under reducing conditions are complex, and uranyl carbonates are the most stable.

Uranium from phosphate fertilizer, $_{\text{ess}}\text{U}$, has been added to the agricultural fields for a long time. Therefore, $_{\text{ess}}\text{U}$ would have partially leached to a deeper layer of a soil or been removed by drainage water. Interestingly, Takeda et al. (2006) reported that $_{\text{ess}}\text{U}$ was retained in the surface layer of the upland field soils. Thus, even under oxic conditions, $_{\text{ess}}\text{U}$ can be found in the soil surface layer, that is, in the crop root zone. For the case of Th, the concentration might also slightly increase due to fertilizer application although the increment would be smaller than that of $_{\text{ess}}\text{U}$. Takeda

Table 2 Concentrations of U and Th and U/Th ratios in bedrocks and nonagricultural soils in Japan

Bedrock ^a	Prefecture	Th, mg kg ⁻¹	U, mg kg ⁻¹	U/Th	References	RM ^b
Andesite	Kanagawa	0.82	0.34	0.41	AIST (2018)	JA-1
	Kagawa	5.03	2.21	0.44	AIST (2018)	JA-2
	Gunma	3.25	1.18	0.36	AIST (2018)	JA-3
	Akita	3.14	0.78	0.25	Ebihara et al. (1984)	
	Niigata	8.59	1.54	0.18	Ebihara et al. (1984)	
	Kagoshima	8.78	2.05	0.23	Tezuka (1972)	
	Akita	3.90	1.18	0.30	Shibata and Nakamura (1997)	
	GM^c	3.84	1.14	0.30		
Soil from andesite		5.62	1.53	0.27	Minato (2005)	
Basalt	Nagasaki	9.30	1.67	0.18	AIST (2018)	JB-1
	Tokyo	0.35	0.18	0.51	AIST (2018)	JB-2
	Yamanashi	1.27	0.48	0.38	AIST (2018)	JB-3
	Akita	6.98	1.70	0.38	Ebihara et al. (1984)	
	Iwate	0.24	0.08	0.32	Shibata and Nakamura (1997)	
	Yamagata	0.40	0.09	0.22	Shibata and Nakamura (1997)	
	Akita	0.57	0.18	0.32	Shibata and Nakamura (1997)	
	Akita	0.48	0.17	0.34	Shibata and Nakamura (1997)	
	Yamagata	3.90	1.11	0.28	Shibata and Nakamura (1997)	
	Akita	6.22	1.74	0.28	Shibata and Nakamura (1997)	
	Hokkaido	1.67	0.51	0.31	Shibata and Nakamura (1997)	
	GM	1.37	0.41	0.31		
Soil from basalt		3.88	0.97	0.25	Minato (2005)	
Rhyolite	Nagano	26.7	8.88	0.33	AIST (2018)	JR-1
	Nagano	31.4	10.9	0.35	AIST (2018)	JR-2
	Kouchi	112	21.1	0.19	AIST (2018)	JR-3
	Gifu	12.3	2.88	0.23	Tezuka (1972)	
	Miyagi	7.5	1.63	0.22	Ebihara et al. (1984)	
	GM	24.4	6.26	0.26		
Soil from rhyolite		8.95	2.33	0.26	Minato (2005)	
GD ^d	Gunma	13.2	3.47	0.26	AIST (2018)	JG-1
GR ^e	Gifu	31.6	11.3	0.36	AIST (2018)	JG-2
GD	Shimane	8.3	2.21	0.27	AIST (2018)	JG-3
GD	Kagoshima	15.5	5.58	0.35	Tezuka (1972)	
GR	Gifu	24.0	4.10	0.17	Katoh et al. (1985)	
GR	Ibaraki	13.0	1.90	0.15	Katoh et al. (1985)	
	GM	16.0	3.94	0.25		
Soil from GD ^d and GR ^e		15.3	3.03	0.20	Minato (2005)	
Limestone	Hokkaido	0.03	1.75	61	AIST (2018)	JLs-1
Dolomite	Tochigi	0.04	0.86	20	AIST (2018)	JDo-1
Slate	Miyagi	9.97	2.63	0.26	AIST (2018)	JSI-1
Slate	Miyagi	11.5	2.92	0.25	AIST (2018)	JSI-2

(continued)

Table 2 (continued)

Bedrock ^a	Prefecture	Th, mg kg ⁻¹	U, mg kg ⁻¹	U/Th	References	RM ^b
Chert	Tochigi	0.74	0.74	1.0	AIST (2018)	JCh-1
Shale	Akita	3.11	2.09	0.67	Kimura et al. (2003)	
Shale	Akita	3.45	6.48	1.9	Kimura et al. (2003)	
Shale	Akita	6.74	2.58	0.38	Kimura et al. (2003)	
	GM	1.29	2.04	1.58		
Soil from sedimentary rock		7.63	1.83	0.24	Minato (2005)	

^aBedrock types were (1) volcanic, andesite, basalt, and rhyolite; (2) plutonic, granodiorite and granite; and (3) sedimentary, limestone, dolomite, slate, chert, and shale

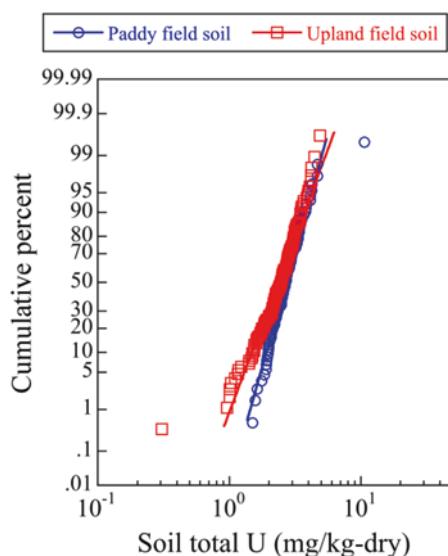
^bRM reference material code

^cGM geometric mean

^dGD granodiorite

^eGR granite

Fig. 5 Distribution of total U concentrations in agricultural soil samples



et al. (2006) showed an example of this phenomenon. Therefore, to estimate $_{ess}U$ concentration, we assumed that excess Th from fertilizers was negligible and thus all Th was initial Th in the soil.

Using Eq. (1), $_{ess}U$ concentration in each soil sample was estimated. For some soil samples, calculated $_{ess}U$ was negative; thus the data were removed. Although the distributions of $_{ess}U$ concentrations in two soil uses did not fit to log-normal curves well (Fig. 6), we could compare the data with total U, GM values, geometric standard deviation (GSD), and ranges that are listed in Table 3. Estimated $_{ess}U$ in upland field and paddy field soil samples were not significantly different by t-test. The GM

Fig. 6 Distributions of estimated $_{\text{ess}}\text{U}$ concentrations in agricultural soil samples

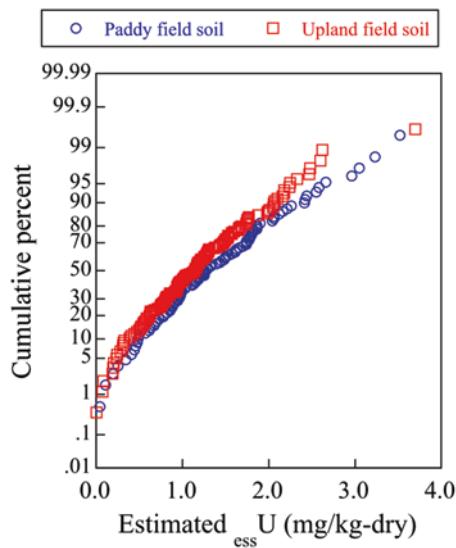


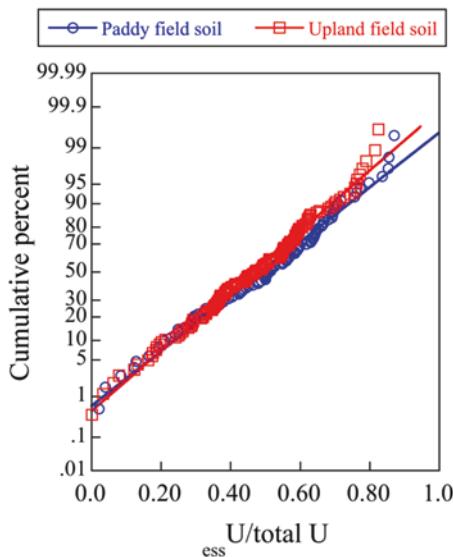
Table 3 Concentrations of total uranium and estimated $_{\text{ess}}\text{U}$ ($\text{mg kg}^{-1}\text{-dry}$) in agricultural soil samples

Soil use	Total or excess	N	U concentrations			
			GM	GSD	Min.	Max.
Paddy field	Total U	98	2.70×10^0	1.3	1.50×10^0	1.06×10^1
	$_{\text{ess}}\text{U}$	95	1.15×10^0	2.0	4.30×10^{-2}	3.52×10^0
Upland field	Total U	139	2.35×10^0	1.5	3.07×10^{-1}	4.89×10^0
	$_{\text{ess}}\text{U}$	132	9.50×10^{-1}	2.3	4.32×10^{-3}	3.70×10^0

value of $_{\text{ess}}\text{U}$ in paddy field soil samples was $1.15 \text{ mg kg}^{-1}\text{-dry}$ and that in upland field soil samples was $0.95 \text{ mg kg}^{-1}\text{-dry}$.

To calculate $_{\text{ess}}\text{U}$ contribution to U in paddy field and upland field soil samples, the concentration ratio between $_{\text{ess}}\text{U}$ to total U was then calculated for each soil sample. The $_{\text{ess}}\text{U}$ /total U ratios are distributed normally for both paddy field and upland field soil samples as shown in Fig. 7. The arithmetic mean values and one sigma errors of $_{\text{ess}}\text{U}$ /total U were 0.49 ± 0.20 for paddy field soil samples and 0.46 ± 0.18 for upland field soil samples. Thus, from these results, on average it was implied that about half of the total U was from U in phosphate fertilizers applied to the paddy field and upland field soil samples.

Fig. 7 Distributions of concentration ratios of $_{\text{ess}}\text{U}$ /total U in agricultural field soil samples



3 Correlations Between U in Crops and $_{\text{ess}}\text{U}$ in Corresponding Agricultural Soils

3.1 Concentrations of U in Crops

Uranium concentrations in edible part of crops (98 rice samples and 147 upland field crop samples) were measured using ICP-MS. Details of the method are found in our previous paper (Uchida et al. 2007a). Although ICP-MS has a low detection limit, U concentrations were under the detection limit in 15 samples; these data were removed from further analysis. Table 4 shows the U concentration data for crops and their categorized groups. Brown rice is hulled rice of *Oryza sativa* (japonica type), and white rice is obtained by polishing the rice grain by removing rice bran (ca. 9% of the total grain weight). The U concentration in each group is summarized in Fig. 8. Although rice and potato are cereals and tubers, respectively, numbers of samples for these crops were large so that they were plotted individually. Loose-leaf-type vegetables showed higher U concentration than other crops, while white rice showed the lowest.

3.2 Correlations Between U in Crops and $_{\text{ess}}\text{U}$ in Soil

It has been reported that U from phosphate fertilizer is soluble in water (Tsumura and Yamasaki 1993; Zielinski et al. 2000). If U is in soluble form, it is easily taken up by plant roots (Dushenkov et al. 1997; Soudek et al. 2011). This means that $_{\text{ess}}\text{U}$

Table 4 Uranium concentrations (mg kg⁻¹-dry) in crop samples collected in Japan

Crop group and English name	Scientific name	N	GM	GSD	Min.	Max.
<i>Cereals</i>						
Brown rice (hulled rice)	<i>Oryza sativa</i> L.	98	1.28×10^{-4}	2.2	2.11×10^{-5}	9.51×10^{-4}
White rice (polished rice)	<i>Oryza sativa</i> L.	91	8.74×10^{-5}	1.9	1.63×10^{-5}	8.87×10^{-4}
Others (wheat, barley)	<i>Triticum</i> L., <i>Hordeum vulgare</i> L.	7	2.63×10^{-4}	3.8	6.22×10^{-5}	2.94×10^{-3}
<i>Leafy vegetables (head or bulb type)</i>						
Cabbage	<i>Brassica oleracea</i> L. var. <i>capitata</i>	9	4.66×10^{-4}	2.1	1.83×10^{-4}	1.56×10^{-3}
Chinese cabbage	<i>Brassica rapa</i> L. var. <i>pekinensis</i>	7	6.27×10^{-4}	2.0	2.41×10^{-4}	1.53×10^{-3}
Others (lettuce, onion)	<i>Lactuca sativa</i> L., <i>Allium cepa</i> L.	5	3.41×10^{-4}	2.7	6.57×10^{-5}	8.39×10^{-4}
<i>Leafy vegetables (loose-leaf type)</i>						
Spinach	<i>Spinacia oleracea</i> L.	6	6.12×10^{-3}	2.1	2.70×10^{-3}	1.79×10^{-2}
Japanese leek	<i>Allium fistulosum</i> L.	13	1.79×10^{-3}	3.8	2.59×10^{-4}	2.35×10^{-2}
Others (carrot leaves, green pak choi, Japanese radish leaves, Nozawana, Takana)	<i>Daucus carota</i> subsp. <i>sativus</i> , <i>Brassica rapa</i> L. var. <i>chinensis</i> , <i>Raphanus sativus</i> L. var. <i>longipinnatus</i> , <i>Brassica rapa</i> L. var. <i>hakabura</i> , <i>Brassica juncea</i> L. var. <i>integerrifolia</i>	5	1.07×10^{-2}	4.1	1.69×10^{-3}	8.76×10^{-2}
<i>Fruit vegetables</i>						
Cucumber	<i>Cucumis sativus</i> L.	4	4.71×10^{-4}	1.5	2.98×10^{-4}	7.38×10^{-4}
Eggplant	<i>Solanum melongena</i>	4	2.57×10^{-4}	1.9	1.11×10^{-4}	5.26×10^{-4}
Others (bitter melon, sweet pepper, tomato)	<i>Momordica charantia</i> L. var. <i>pavel</i> Crantz, <i>Capsicum annuum</i> L. var. <i>grossum</i> , <i>Solanum lycopersicum</i> L.	5	4.26×10^{-4}	4.1	8.61×10^{-5}	1.46×10^{-3}
<i>Root vegetables</i>						
Japanese radish	<i>Raphanus sativus</i> L. var. <i>longipinnatus</i>	7	9.49×10^{-4}	2.2	2.54×10^{-4}	2.35×10^{-3}
Carrot	<i>Daucus carota</i> subsp. <i>sativus</i>	3	1.46×10^{-3}	3.7	4.23×10^{-4}	5.86×10^{-3}
<i>Beans</i>						
Soybean	<i>Glycine max</i>	6	4.77×10^{-4}	2.2	1.68×10^{-4}	1.24×10^{-3}
<i>Tubers</i>						
Potato	<i>Solanum tuberosum</i> L.	46	5.83×10^{-4}	2.5	6.85×10^{-5}	6.43×10^{-3}
Others (sweet potato, taro)	<i>Ipomoea batatas</i> L., <i>Colocasia esculenta</i>	5	1.58×10^{-3}	2.8	3.97×10^{-4}	4.56×10^{-3}

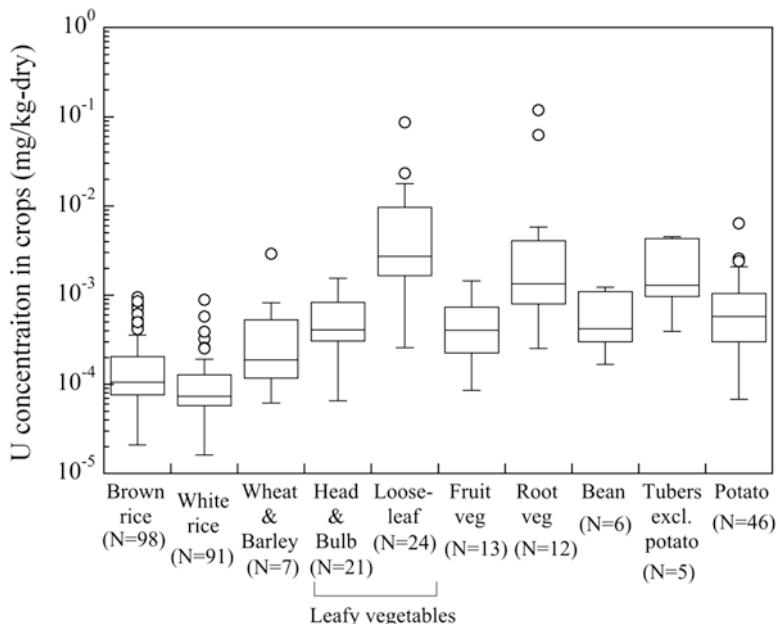


Fig. 8 Box plots of the uranium concentrations in ten crop groups

might be readily available to plants; therefore, we hypothesized that $_{\text{ess}}\text{U}$ concentration in soils and U in crops grown in the soils would be positively correlated, if $_{\text{ess}}\text{U}$ was in soluble forms in soil after its application. Among the crops we used in this study, there were large numbers of brown rice ($N = 98$) and potato ($N = 46$) samples. Thus, using their data sets, we analyzed their correlations.

The results are shown in Fig. 9. From these figures and statistical analyses, we confirmed that there were no correlations between crop U concentrations and $_{\text{ess}}\text{U}$ in soil. We also found that total U concentration did not have any correlations, as Vandenhove et al. (2007) suggested. They reported that it was difficult to predict U concentrations in plants from the total U and the water-soluble U concentrations; although to their multiple linear regression analysis they added data related to the U species, those species which were probably the uranyl species that are most readily taken up by plants, the results still provided poor correlation with the observed TF ($R = 0.65$). The results implied that added U was not bioavailable and thus should have affected little in U concentration in crops.

However, if the $_{\text{ess}}\text{U}$ amount was higher or lower compared to that of the initial U ($_{\text{init}}\text{U}$) in soil, U transfer to crops might be affected because of the different physico-chemical forms of $_{\text{ess}}\text{U}$ and $_{\text{init}}\text{U}$. To ignore the total U concentration effect, the values of TF defined as “concentration of U in crop (mg kg⁻¹-dry)/concentration of U in soil (mg kg⁻¹-dry)” were calculated, and then selected data were categorized into two groups, that is, a concentration ratio of $_{\text{ess}}\text{U}/_{\text{init}}\text{U}$ of (1) more than 2 and (2) less than 0.5. TF results for brown rice and potato were used for this analysis and they

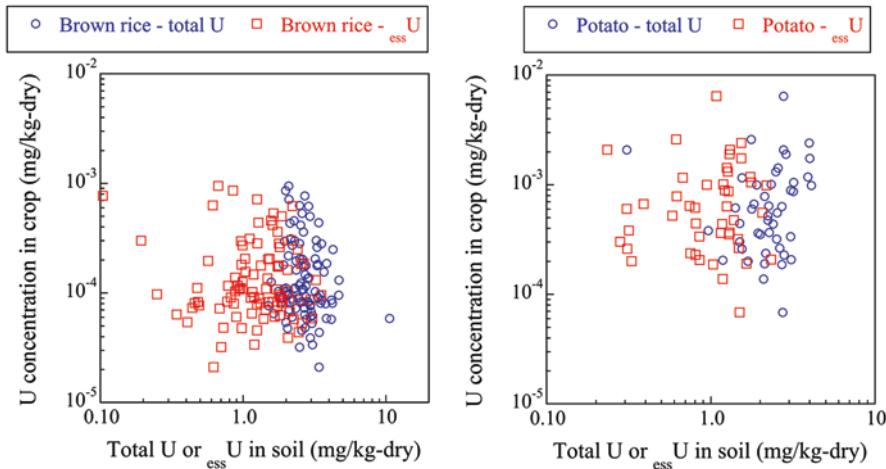


Fig. 9 Correlations between U in crops and total U or _{ess} U in agricultural soil samples

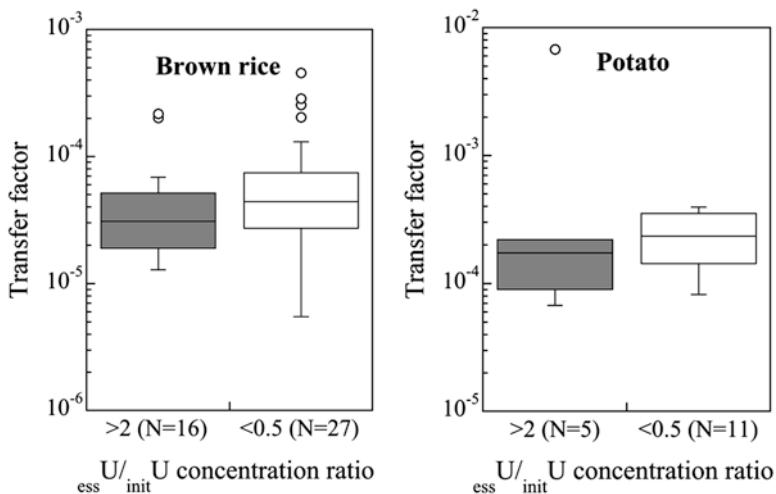


Fig. 10 Comparison between TFs of high and low _{ess} U/_{init} U concentration ratios in soil samples

are shown in Fig. 10. For both crops, even if _{ess} U values were two or more times higher than _{init} U values in soil samples (_{ess} U/_{init} U > 2), the TF values did not differ from the low _{ess} U case (_{ess} U/_{init} U < 0.5) by *t*-test. Therefore, we could conclude that the newly added U by phosphate fertilizer was not more bioavailable than initially existing U in the soil. The results indicated that in the soil-to-crop environment, U from radioactive disposal sites and _{init} U will behave similarly. Thus, we can use TF values of U obtained from field studies for long-term dose assessment.

4 Soil-to-Crop Transfer Factor of U from a Field Study

From the above discussion, we saw that TF values of U can be obtained using field observation results. Therefore, in Table 5, we summarized our data obtained from a field study by collecting crops (edible parts) and their corresponding soil samples at harvest throughout Japan. We have reported some TF values of U elsewhere (Uchida et al. 2007a, 2007b; Tagami et al. 2009), but in Table 5, by adding some data that we recently obtained and also previously reported (Komamura and Tsumura 1994; Tsukada and Nakamura 1998; Sasaki et al. 2002), TFs for the ten crop groups as listed in Table 4 are shown.

Generally, data for leafy vegetables have been categorized as one group (IAEA 2010) which made the TF range wide (7.8×10^{-5} to 8.8) with a large GSD of 7.3; this could cause large uncertainty for the dose assessment. In this work, therefore, we separated leafy vegetables into two types, that is, head and bulb type and loose-leaf type. For loose-leaf-type vegetables, the TF values were significantly higher than those for head- and bulb-type vegetables by *t*-test ($p < 0.001$). If we combined these data into one leafy vegetable group, then the GM was 5.99×10^{-4} with GSD of 4.9. Thus separating into these two categories could make the uncertainties smaller. It would be better to classify crop types by their functions.

5 Conclusions

For environmental dose assessment from radioactive waste disposal sites, it is necessary to use soil-to-crop transfer factors (TFs) in mathematical models. For the case of U, it might be possible to obtain TFs by measuring naturally existing U in agricultural fields and crops; however, initially existing U in soil and added U from radioactive waste might behave differently because of their different chemical forms. Therefore, in this study, we focused on added U from phosphate fertilizers applied to the agricultural fields, for both paddy field and upland field conditions.

Table 5 Soil-to-crop transfer factor of uranium for ten crop groups

Crop group	N	GM	GSD	Min.	Max.
Brown rice	99	4.80×10^{-5}	2.4	5.52×10^{-6}	4.57×10^{-4}
White rice	92	3.27×10^{-5}	2.2	4.23×10^{-6}	3.36×10^{-4}
Wheat and barley	7	9.78×10^{-5}	3.7	2.58×10^{-5}	9.84×10^{-4}
Head and bulb type	23	1.78×10^{-4}	2.6	1.89×10^{-5}	1.49×10^{-3}
Loose-leaf type	25	1.70×10^{-3}	3.7	1.67×10^{-4}	2.84×10^{-2}
Fruit vegetables	13	1.51×10^{-4}	2.6	3.16×10^{-5}	7.28×10^{-4}
Root crops	12	8.17×10^{-4}	6.8	8.95×10^{-5}	3.53×10^{-2}
Bean	6	1.79×10^{-4}	2.1	6.12×10^{-5}	4.46×10^{-4}
Tuber excl. potato	5	6.99×10^{-4}	3.5	1.82×10^{-4}	3.69×10^{-3}
Potato	47	2.63×10^{-4}	2.6	2.51×10^{-5}	6.79×10^{-3}

Although redox conditions in paddy fields and upland field should be different and that might affect U physicochemical forms in soil, it was implied that there was no TF difference between initially existing U in soil and added U (_{ess}U) in soil-to-rice and soil-to-potato systems. Thus, we concluded that TF values of U obtained from field studies are applicable for long-term radiation dose assessment.

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Influence of Uranium Speciation on Plant Uptake



Nan Hu, Hui Zhang, Dexin Ding, Yujian Tan, and Guangyue Li

Abstract Firstly, in order to confirm the proportions of different species of uranium in solutions at different pH levels, carbonate and phosphate concentrations were calculated through Visual MINTEQ 3.1 software. Then, based on the calculation results, solutions with different species of uranium were prepared. Finally, the accumulation behavior of different species of uranium by *Azolla-Anabaena* was studied through hydroponic experiments. The results show that the growth inhibition rates on *Azolla-Anabaena* by these species of uranium were significantly different. UO_2^{2+} , $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, and $(\text{UO}_2)_3(\text{OH})_5^+$ species inhibited its growth, but UO_2PO_4^- promoted its growth. The bioaccumulation amounts of these species of uranium by *Azolla-Anabaena* were significantly different, too. In order to increase the bioaccumulation amounts of uranium by *Azolla-Anabaena*, the main species of uranium in solution should be regulated to UO_2^{2+} or $(\text{UO}_2)_3(\text{OH})_5^+$, and the concentrations of carbonate and phosphate in the medium should be reduced.

Keywords Phytoremediation · Uranium · Speciation · Bioaccumulation

1 Introduction

Phytoextraction is a process that includes the uptake of elemental/compound by plant roots from the contaminated soil and water and translocation and accumulation of the elemental/compound into plant shoots and leaves. The uranium species in solution have great influence on the bioaccumulation of uranium by plant (Markich 2002). The predominant uranium species in aqueous solutions are UO_2^{2+} under low pH conditions, which is stable and can migrate freely (Ragnarsdottir and Charlet 2000; Song et al. 2012). With the increase of pH, the UO_2^{2+} in the aqueous solution tends to be hydrolyzed to the hydroxide complex $\text{UO}_2(\text{OH})_x$ (Ebbs et al. 1998). Lee and Yang (2010) reported the phytoremediation of different uranium

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species mediated by pH in groundwater by sunflowers and peas. The results showed that the phytoremediation efficiency of uranium by these two plants became the highest at pH 3~5, and it exceeded 90%. Inorganic anions, such as carbonates, phosphates, natural organic acids, etc., tended to form complexes with uranium, which affected the uptake of uranium by plants (Nakajima et al. 1979; Greene et al. 1986; Srivastava et al. 2010; Laurette et al. 2012a; Li and Zhang 2012; Pratas et al. 2012, 2014; Nie et al. 2014; Pan et al. 2016). Greene et al. (1986) and Nakajima et al. (1979) reported that with the increase of carbonate concentration, the amount of the adsorbed uranium by single-cell algae (*C. regularis* and *C. vulgaris*) gradually decreased. When phosphate was present in the solution, it reacted with uranium to form a precipitate, and the bioaccumulation of uranium decreased (Mkandawire et al. 2007; Misson et al. 2009).

Azolla-Anabaena is a kind of fern-algae symbiotic aquatic plant and has been used as green manure in rice fields, due to its strong nitrogen fixation ability (Tang et al. 2000). Arora et al. (2006) and Rai (2008) have found that *Azolla-Anabaena* had strong accumulation ability for heavy metals in solutions. Other studies have also showed that *Azolla-Anabaena* had a strong accumulation capability for uranium. Hu et al. (2012) have found that *Azolla-Anabaena* symbiotic system had excellent performance for removal of uranium. Heavy metal and uranium accumulation by *Azolla-Anabaena* has been reported extensively; however, the accumulation behavior of different uranium species by *Azolla-Anabaena* has not been studied. In this paper, the proportions of different species of uranium in solutions under different conditions were calculated with MINTEQ 3.1 software, which is a chemical equilibrium computer program that has an extensive thermodynamic database enabling users to calculate the speciation, solubility, and equilibrium of solid and dissolved phases of minerals in an aqueous solution (Gustafsson 2006). Based on the calculation results, five solutions containing UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, and UO_2PO_4^- , respectively, were prepared. The effects of uranium speciation on the bioaccumulation by and translocation in *Azolla-Anabaena* were finally investigated through hydroponic experiments, and the new ideas and theoretical basis for further improving the removal efficiency of uranium by *Azolla-Anabaena* from water were provided.

2 Material and Methods

2.1 Material

Azolla-Anabaena was taken from a field in the suburb of Hengyang city in South China. After the *Azolla-Anabaena* was washed with tap water for 3~5 min, it was put into the improved Hoagland nutrient solution and cultivated for 2 weeks for experimentation (Hu et al. 2012).

2.2 Hydroponic Experiment

Experiments were conducted using 3 L beakers, which were divided into six groups, including five experimental groups (A, B, C, D, and E) and one control group (F). The $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into each experimental group, and its initial uranium concentration was set at 2 mg L^{-1} . The experiments were conducted in triplicate. Each beaker in all groups contained 3 g of *Azolla-Anabaena* and 1 L Hoagland nutrient solution. The pH values of groups A, B, and C were adjusted to 4.0, 6.5, and 10.5, respectively, by HCl and NaOH. A 10 mM Na_2CO_3 and 1 mM K_2HPO_4 were added into groups D and E, respectively. The beakers for experiments were put into the climate box. The temperature was set at 25°C during the day and 22°C during the night, and the air humidity was maintained at 80%. The day and night ratio was set at 12:12. The uranium contents and their removal rates were measured every 3 days. The fresh weights were analyzed after 15 days, and the growth inhibition rates (G) were calculated using the following formula:

$$G = (g_0 - g_1) / g_0 \times 100\% \quad (1)$$

where G is the growth inhibition rate (percent), g_0 is the fresh weight of the *Azolla-Anabaena* in the control group (g), and g_1 is the fresh weight of the *Azolla-Anabaena* in the experimental group (g).

2.3 Preparation of Different Species of Uranium

Visual MINTEQ 3.1 Software

The proportions of different species of uranium in solutions under different conditions were calculated with MINTEQ 3.1 software. In a typical experimental process, once Visual MINTEQ is started, the main menu will appear. Then, change the pH option to “Fixed at,” and make sure that the value in the text box is 4.0. The ionic strength option should be “To be calculated,” since it is the default option. The concentration unit should be mg L^{-1} , and the temperature is given as 25°C . Then add the component, U(VI), with a concentration of mg L^{-1} . Next, click “Run” to calculate the proportions of different species of uranium.

Preparation of UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, and $\text{UO}_2(\text{OH})_3^-$

In order to confirm the experimental conditions needed for different species of uranium and the proportions of different species of uranium in solutions at different pH levels, carbonate and phosphate concentrations were calculated by Visual MINTEQ 3.1 software, which were calculated by the software when the initial uranium concentration was 2 mg L^{-1} (Fig. 1). As shown in the figure, the main species of

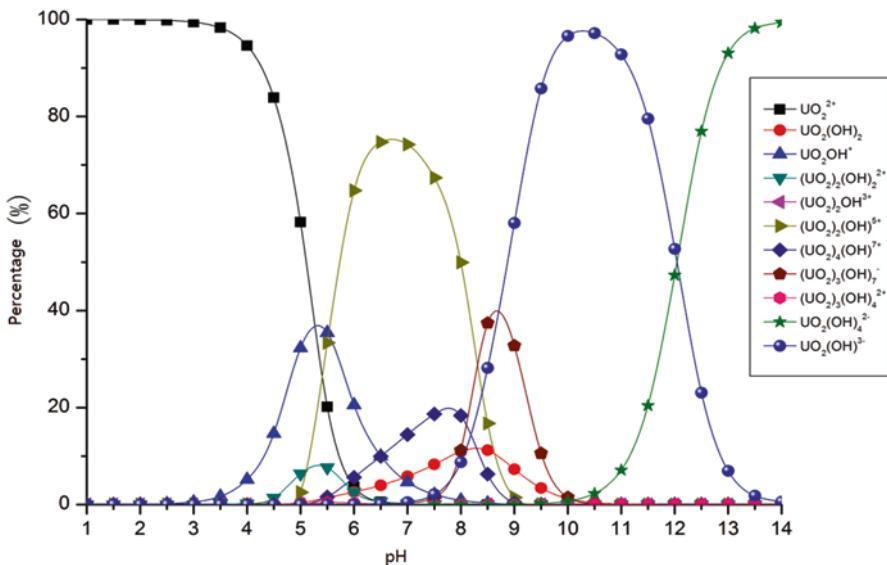


Fig. 1 Simulated variation of percentages of different species of uranium in deionized water with pH (the total concentration of uranium is 2 mg L⁻¹)

uranium in solution was UO_2^{2+} when the pH value was below 5, while when the pH value was between 8.5 and 12, the main species of uranium in solution was $\text{UO}_2(\text{OH})_3^-$. The maximum proportion of UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, and $\text{UO}_2(\text{OH})_3^-$ in solutions reached 99.99, 74.73, and 97.2%, respectively, when the pH value was 1.0, 6.5, and 10.5, respectively. However, our pre-experimental results showed that *Azolla-Anabaena* could not survive for more than 10 days when the pH value was below 2.5. Therefore, the pH value for hydroponic experiments cannot be set at 1.0. The survival duration of *Azolla-Anabaena* was greatly prolonged when the pH value was 4.0. At the same time, the main species of uranium in solution was also UO_2^{2+} , and its proportion reached 94%. Thus, UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, and $\text{UO}_2(\text{OH})_3^-$ were selected as three different species of uranium for the hydroponic experiments, and the corresponding pH values in the solutions were 4, 6.5, and 10.5 respectively.

Preparation of $\text{UO}_2(\text{CO}_3)_3^{4-}$ and UO_2PO_4^-

The proportions of different species of uranium in solutions at different carbonate and phosphate levels were calculated by the software when the initial uranium concentration was 2 mg L⁻¹ and the pH value was 7 (Fig. 2). As shown in Fig. 2, the proportion of different species of uranium in the solution varied with the increase of carbonate concentration. The main species of uranium in solution was $\text{UO}_2(\text{CO}_3)_3^{4-}$, and its proportion reached 70.33%, when the carbonate concentration was 10 mM. The main species of uranium in solution was UO_2PO_4^- , when the phosphate concentration was above 0.2 mM. The maximum proportion of UO_2PO_4^- in solution

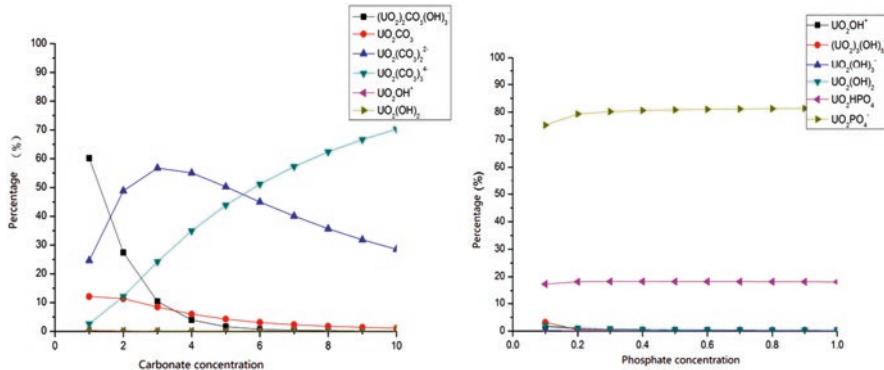


Fig. 2 Simulated variation of percentages of different species of uranium in deionized water with the concentration of phosphate or carbonate at pH = 7 (total concentration of U is 2 mg L⁻¹).

reached 80%, when the phosphate concentration was above 1.0 mM. Thus, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and UO_2PO_4^- were selected as other two different species of uranium for the hydroponic experiments, and the corresponding pH values in the solutions were 7; carbonate and phosphate concentrations were 10 and 1 mM, respectively.

2.4 Bioaccumulation Amount and Bioaccumulation Factor

The uranium contents in the *Azolla-Anabaena* were analyzed after 15 days, and the bioaccumulation factors (BAFs) were used to assess the capacity of *Azolla-Anabaena* to accumulate and transport uranium, and they were calculated by the following formula:

$$\text{BAFs} = \frac{C_{\text{plant}}}{C_{\text{water}}} \quad (2)$$

where C_{plant} is the uranium content in the *Azolla-Anabaena* (mg kg⁻¹ in dry weight) and C_{water} is the uranium content in the soil (mg kg⁻¹).

3 Results and Discussion

3.1 Growth Inhibition Rates on the *Azolla-Anabaena* Under Stresses of Different Species of Uranium

The growth inhibition rates on the *Azolla-Anabaena* under the stresses of five solutions of uranium species with the uranium concentration of 2 mg L⁻¹ were calculated (Fig. 3). As shown in Fig. 3, the growth of *Azolla-Anabaena* was inhibited

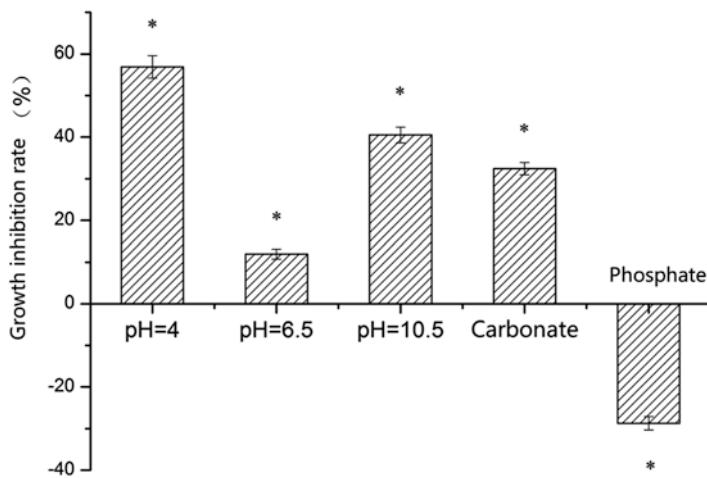


Fig. 3 Growth inhibition rates on *Azolla-Anabaena* under stresses of uranium solutions with uranium concentration of 2 mg L^{-1}

significantly by UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, $\text{UO}_2(\text{OH})_3^-$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The growth inhibition effect of the species of uranium in solution was in the order $\text{UO}_2^{2+} > \text{UO}_2(\text{OH})_3^- > (\text{UO}_2)_3(\text{OH})_5^+ > \text{UO}_2(\text{CO}_3)_3^{4-}$. The maximum growth inhibition rate on *Azolla-Anabaena* reached 56.87%, when the main species of uranium in the solution was UO_2^{2+} . The minimum growth inhibition rate on *Azolla-Anabaena* reached 11.96%, when the main species of uranium in the solution was $(\text{UO}_2)_3(\text{OH})_5^+$. However, the growth of the *Azolla-Anabaena* was promoted significantly by UO_2PO_4^- , and the growth promotion rate reached 28.71%. This is because the addition of phosphorus in solution can significantly promote the growth of *Azolla-Anabaena* (Chen 2003). To summarize, the growth inhibition rates on *Azolla-Anabaena* were significantly different under the stresses of five species of uranium in solution; UO_2^{2+} , $(\text{UO}_2)_3(\text{OH})_5^+$, $\text{UO}_2(\text{OH})_3^-$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ could inhibit the growth of *Azolla-Anabaena*, while UO_2PO_4^- could promote the growth of *Azolla-Anabaena*.

3.2 Variation of Uranium Concentrations in Different Hydroponic Solutions

The concentrations of uranium in five solutions of uranium species with the uranium concentration of 2 mg L^{-1} for the cultivation of *Azolla-Anabaena* were analyzed (Fig. 4). As shown in Fig. 4, the concentration of uranium in hydroponic solution decreased by about 3/4 in the first 3 days, and the decline of uranium concentration became slow when the main species of uranium in the solutions were UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_5^+$. The minimum concentration of uranium in hydroponic

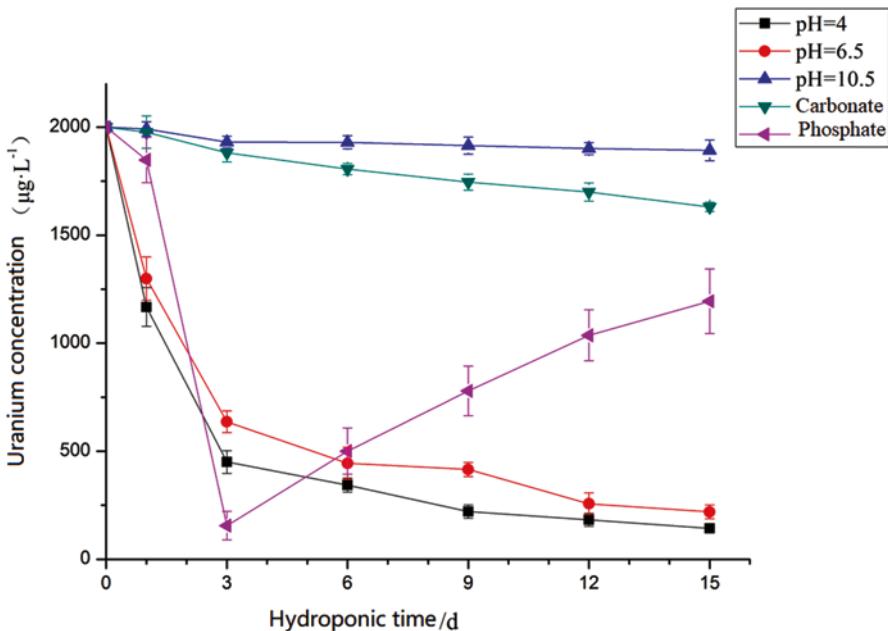


Fig. 4 Variation of uranium concentrations in different hydroponic solutions where *Azolla-Anabaena* was cultivated

solution was $143 \mu\text{g L}^{-1}$, and the removal rate of uranium by *Azolla-Anabaena* reached 92.9% after 15 days of hydroponic experiment when the main species of uranium in the solutions was UO_2^{2+} . The concentration of uranium in hydroponic solution was also very low, which reached $220 \mu\text{g L}^{-1}$ when the main species of uranium in the solutions was $(\text{UO}_2)_3(\text{OH})_5^+$. These results indicated that the removal rate by *Azolla-Anabaena* was very high when the main species of uranium in the solutions were UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_5^+$. This is because UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_5^+$ were both metal cations which can easily be absorbed by *Azolla-Anabaena*.

The concentrations of uranium in hydroponic solution were very high, and the decline rate of uranium concentration was very small in the 15 days of the hydroponic experiment when the main species of uranium in the solutions were $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The uranium concentrations in the final solution were $1892 \mu\text{g L}^{-1}$ and $1631 \mu\text{g L}^{-1}$, respectively, and the removal rates of uranium by *Azolla-Anabaena* were only 5.4% and 18.5%, respectively. The results indicated that the removal rates of uranium by *Azolla-Anabaena* were very low when the main species of uranium in the solutions were $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The reason is that $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ were both metal anions which cannot easily be absorbed by *Azolla-Anabaena*.

The minimum concentrations of uranium in hydroponic solution reached $156 \mu\text{g L}^{-1}$ at the third day, and the uranium concentration gradually increased to $1194 \mu\text{g L}^{-1}$ at the fifteenth day, when the main species of uranium in the solutions

was UO_2PO_4^- . The uranium concentration was reduced to the lowest level at the third day because of the precipitation of phosphate and uranium. After that, the reason for uranium concentration increase may be that *Azolla-Anabaena* secreted organic acids (Rauser 1999; Bertin et al. 2003; Huang et al. 2016) in its roots during growth, and the complexes formed by phosphate and uranium were dissolved in solution again. Thus, in order to increase bioaccumulation amounts of uranium in *Azolla-Anabaena*, the main species of uranium in solution should be regulated to UO_2^{2+} or $(\text{UO}_2)_3(\text{OH})_5^+$, and the concentrations of carbonate and phosphate in medium should be reduced.

3.3 Bioaccumulation Amount and Bioaccumulation Factor of *Azolla-Anabaena* for Uranium in Different Hydroponic Solutions

The bioaccumulation amount and bioaccumulation factor of *Azolla-Anabaena* for uranium in different hydroponic solutions were calculated (Table 1). As shown in Table 1, the maximum bioaccumulation amount and bioaccumulation factor of five different uranium species by *Azolla-Anabaena* reached 3831 and 1916 mg kg^{-1} , respectively, when the main species of uranium in the solutions was UO_2^{2+} . The results indicated that the bioaccumulation ability of *Azolla-Anabaena* for UO_2^{2+} was the highest among five different uranium species in the hydroponic experiments. The bioaccumulation amount and bioaccumulation factor of *Azolla-Anabaena* for $(\text{UO}_2)_3(\text{OH})_5^+$ were 3057 and 1529 mg kg^{-1} , respectively. The bioaccumulation amount and bioaccumulation factor for $(\text{UO}_2)_3(\text{OH})_5^+$ were nearly the same as for UO_2^{2+} , which indicated that *Azolla-Anabaena* also had high ability to accumulate $(\text{UO}_2)_3(\text{OH})_5^+$. The reason was that UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_5^+$ were both metal cations which can easily be absorbed by *Azolla-Anabaena*. The influences of uranium speciation on the accumulation and translocation in oilseed rape, sunflower, and wheat were studied by Laurette et al. (2012b). They found that bioaccumulation amounts in the roots of oilseed rape, sunflower, and wheat were all very high when the main species in the solution was UO_2^{2+} (Laurette et al. 2012b). The effects of UO_2^{2+} ,

Table 1 Bioaccumulation amount and bioaccumulation factor of *Azolla-Anabaena* for uranium in different hydroponic solutions

Initial uranium concentration (mg L^{-1})	Condition	Bioaccumulation amount (mg kg^{-1})	Bioaccumulation factor
2.0	pH = 4	$3831 \pm 326^*$	1916
	pH = 6.5	$3057 \pm 213^*$	1529
	pH = 10.5	$122 \pm 10^*$	61
	Carbonate	$622 \pm 31^*$	311
	Phosphate	$132 \pm 8^*$	66

* $p < 0.05$

(UO_2)₃(OH)₅⁺, and $\text{UO}_2(\text{OH})_3^-$ in cultivation solution on the uptake of U by variant *Sedum alfredii* were studied by Du et al. (2016). They found three different uranium species would all have significant effect on the uranium bioaccumulation. The bioaccumulation amount in the roots of *Sedum alfredii* reached the highest, which was $3.7 \times 10^4 \text{ mg kg}^{-1}$, when the main species in the solution was (UO_2)₃(OH)₅⁺ (Du et al. 2016). The results reported by Laurette et al. (2012b) and Du et al. (2016) were consistent with our research results.

The minimum bioaccumulation amount and bioaccumulation factor of five different uranium species by *Azolla-Anabaena* reached 122 and 61 mg kg^{-1} , respectively, when the main species of uranium in the solutions was $\text{UO}_2(\text{OH})_3^-$. The bioaccumulation amount and bioaccumulation factor of $\text{UO}_2(\text{CO}_3)_3^{4-}$ by *Azolla-Anabaena* were also very low, which were 622 and 311 mg kg^{-1} , respectively. The results indicated that the bioaccumulation ability of *Azolla-Anabaena* for uranium was inhibited when the main species of uranium were $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. This is because $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ were both metal anions which cannot easily be absorbed by *Azolla-Anabaena*. The results agreed with those by Du et al. (2016) who found that $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ in the solution could inhibit the ability of bioaccumulation of uranium by variant *Sedum alfredii* (Du et al. 2016).

The bioaccumulation amount and bioaccumulation factor of *Azolla-Anabaena* for UO_2PO_4^- were only 132 and 66 mg kg^{-1} , respectively, when the main species of uranium in the solutions was UO_2PO_4^- . The results indicated that the bioaccumulation ability of *Azolla-Anabaena* for uranium was also greatly inhibited when the main species of uranium was UO_2PO_4^- . The reasons for these results are that phosphate and uranium could form an insoluble complex, and the species of UO_2PO_4^- was anionic, which cannot easily be absorbed by *Azolla-Anabaena*. Misson et al. (2009) and Mkandawire et al. (2007) also reported that phosphate could inhibit the ability of plants to accumulate uranium. Thus, in order to increase the removal rate and bioaccumulation amount of uranium by *Azolla-Anabaena*, the main species of uranium in solution should be regulated to UO_2^{2+} or (UO_2)₃(OH)₅⁺, and the concentration of carbonate and phosphate in solution should be reduced.

4 Conclusions

1. The growth inhibition rates on *Azolla-Anabaena* by the five uranium species were significantly different. (UO_2)₃(OH)₅⁺, $\text{UO}_2(\text{OH})_3^-$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ had high growth inhibition, UO_2^{2+} had higher growth inhibition, and UO_2PO_4^- had high growth promotion.
2. The accumulation efficiencies of UO_2^{2+} and (UO_2)₃(OH)₅⁺ by *Azolla-Anabaena* were relatively high; the bioaccumulation amount and bioaccumulation factor of UO_2^{2+} by *Azolla-Anabaena* reached 3831 and 1916 mg kg^{-1} , respectively; and its bioaccumulation amount and bioaccumulation factor for (UO_2)₃(OH)₅⁺ were 3057 and 1529 mg kg^{-1} , respectively.

3. In order to increase the removal rate and bioaccumulation amount of uranium by *Azolla-Anabaena*, the main species of uranium in solution should be regulated to UO_2^{2+} or $(\text{UO}_2)_3(\text{OH})_5^+$, and the concentrations of carbonate and phosphate in solution should be reduced.

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Assessment Modelling and the Evaluation of Radiological and Chemical Impacts of Uranium on Humans and the Environment



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Abstract Models of varying degrees of complexity are used to simulate the transport of uranium through the environment. These models rely heavily on empirical data on soil and sediment distribution coefficients and concentration ratios or transfer factors for biota. The empirical data relevant to modelling uranium transport in both terrestrial and aquatic environments are reviewed, and consideration is given to how either measured or calculated concentrations of uranium in environmental media can be used to evaluate radiotoxic and chemotoxic impacts on human health and the environment.

Keywords Mathematical model · Distribution coefficients · Concentration ratios · Transfer factors · Radiotoxicity · Chemotoxicity · Humans · Environment

1 Introduction

Uranium is present at low concentrations in all environmental media and can occur at high concentrations in specific deposits (Payne and Airey 2006). Over the last several decades, exploitation of those deposits has resulted in extensive contamination of the environment with uranium and its radioactive progeny. In consequence, substantial programmes for the remediation of former uranium mining and milling sites have been put in place. Both in the context of ongoing uranium exploration and exploitation, and in determining preferred options for remediation of previously exploited sites, there is a need to have available methodologies, mathematical models and data that can be used to assess the radiological and chemical impacts of uranium on human health and the environment. In view of these considerations, the International Atomic Energy Agency (IAEA) has initiated preparation of a series of documents covering the environmental behaviour and impacts of radionuclides of the uranium and thorium series. One of those documents (IAEA 2018) relates

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specifically to uranium, and the content of this chapter relies substantially on material included in that document.

To assess the impacts of uranium on human health and the environment, consideration must be given to the source of uranium, its transport pathways through the environment and the receptors (both humans and other types of biota) that may be exposed. Figure 1 illustrates the relevant considerations appropriate to uranium.

Once uranium concentrations in environmental media have been determined, impacts on both human health and the environment can be evaluated. Because uranium is radioactive and chemically toxic, both its radiotoxicity and its chemotoxicity need to be addressed. In practice, either the radiotoxicity or the chemotoxicity can be the more important consideration, depending on factors such as the route of exposure, degree of enrichment or depletion and presence or absence of radioactive progeny (see Sect. 3).

Whether radiotoxicity or chemotoxicity is the primary consideration, and whether the endpoint is protection of human health or the environment, there is a common requirement to determine the concentrations of uranium and its progeny in the environmental media to which the relevant receptors will be exposed. For assessment purposes, it is useful to have a well-defined set of environmental media for which concentrations are measured or calculated. Thus, for example, for human foods, the IAEA plant classification system is based on 14 plant groups, with each group distinguished into up to 10 components. For soils, the FAO/UNESCO soil classification system could be used, but this has 28 units and 125 subunits, and the available, element-specific data are not sufficient to justify use of such a complex

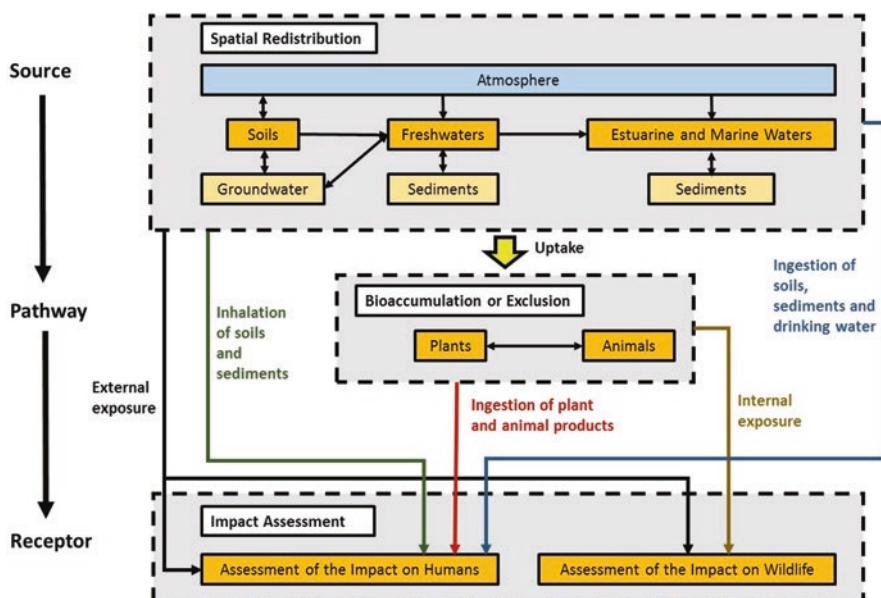


Fig. 1 Source-pathway-receptor analysis appropriate to uranium (IAEA 2018)

classification. Therefore, the IAEA typically uses a much simpler classification scheme based on texture and organic matter content (IAEA 2009, 2010). For uranium, a classification scheme that takes account of pH as well as texture has been found to be useful (see Sect. 2).

In evaluating impacts on non-human biota, it is not possible to address all possible taxa. Therefore, approaches have been developed based on the use of reference organisms (Larsson 2004) or reference animals and plants (RAPs) (ICRP 2007, 2008). In either case, the definitions are similar. Thus, a RAP is defined as *a hypothetical entity, with the assumed basic biological characteristics of a particular type of animal or plant, as described to the generality of the taxonomic level of Family, with defined anatomical, physiological and life-history properties, that can be used for the purposes of relating exposure to dose, and dose to effects, for that type of living organism.* In this context, the IAEA (2014) has produced a handbook on estimating transfers to wildlife that is similar to its handbook on estimating transfers to human foodstuffs (IAEA 2010) and is based on a reference organism concept. The use of a reference organism approach is appropriate to evaluating both the radiological and chemotoxic impacts of uranium.

Models used to simulate the transport of uranium and its progeny in the environment for assessment purposes may be very simple, e.g. they may involve no more than a 1D vertical representation of advection and dispersion in the soil column, with uptake by plants estimated using an empirically derived ratio between the concentration in plants and the concentration in the underlying soil (Thorne 2012, 2014). However, much more complex models may also be used, e.g. 3D coupled representations of water flow, sediment movement and contaminant transport in a surface-water catchment (Bosson et al. 2010). The level of complexity of the assessment model should be matched to the significance of the environmental issue being addressed (e.g. spatial extent and degree to which uranium concentrations are increased above typical background or baseline values) and the need for assurance that the key factors controlling the transport of uranium in the environment are included in the model, so that the robustness of the results obtained can be determined. In some situations, specific aspects may need to be investigated through detailed modelling, in order that a simplified assessment approach can be derived and/or justified (IAEA 2018).

Assessment models are often empirical in nature, i.e. with parameter values based on observed relationships between different environmental media, but without explicit consideration of the processes giving rise to those relationships. Also, in the past, assessment approaches have typically been deterministic, using point estimates of the various parameters. However, there is now an increasing use of probabilistic approaches, with input parameter values selected from specified probability density functions.

In the following sections of this chapter, more detailed consideration is given to the quantification of environmental transfer processes and to the assessment of radiological and chemotoxic impacts of uranium once concentrations in environmental media have either been measured or modelled.

2 Quantification of Environmental Transfer Processes

2.1 General Considerations

Uranium is transported through the environment by various physical, chemical and biological processes. In terrestrial systems, uptakes from soil can result in both radiological and chemical impacts on a wide variety of plants and animals. In the aquatic environment, transport occurs mainly in surface waters, but sorption to suspended and bottom sediments also occurs. As in terrestrial systems, the uptake of uranium into a wide variety of types of biota occurs. Also, some types of biota have mixed terrestrial and aquatic habitats and take up uranium from both types of environment.

2.2 Uptake and Retention in Soils and Sediments

In soils and sediments, a key consideration is the partitioning of uranium between the soil solution and soil solids. Sorption of uranium onto soil solids is usually quantified by use of a distribution coefficient (K_d value) defined as the ratio of the concentration in soil solids to the concentration in solution. This is an equilibrium concept and is an approach often used for indigenous elements (Goody et al. 1995; Sheppard et al. 2011), where it may give larger K_d values than obtained in batch tests with recently added radionuclides, because the indigenous element may be irreversibly sorbed or incorporated into the soil matrix and, therefore, not available for exchange with soil solution.

Uranium sorption is affected by soil properties, mainly pH, content of amorphous iron oxides, soil texture, specific surface area, organic matter content, cation exchange capacity and carbonate and phosphate status (EPA 1999; Payne et al. 2011). Although various regression relationships between K_d and pH have been proposed (Echevarria et al. 2001; Sheppard et al. 2006), these explain a relatively small fraction of the observed variance, and other soil properties need to be considered. The IAEA (2018) suggests that if information on organic matter content and pH are available, a lognormal distribution of K_d values should be used, with the characteristics of the lognormal distribution being as listed in Table 1.

2.3 Uptake and Retention of Uranium in Terrestrial Plants

The IAEA (2010) describes the plant uptake of uranium from soil using the transfer factor, F_v , defined as the ratio of the dry weight concentration in the plants to the dry weight concentration in a specified soil layer (to a depth of 0.1 m in pasture and 0.2 m for other crop types). The inadequacies of the F_v approach are widely

Table 1 $K_d(U)$ (L kg^{-1}) grouped by pH and organic matter criteria (IAEA 2018)

		<i>N</i>	Geometric mean	Geometric standard deviation	5th Percentile	95th Percentile
pH < 5	Mineral	46	115	5.3	7	1765
	Organic	9	580	2.5	130	2575
5 ≤ pH < 7	Mineral	62	900	4.3	80	9930
	Organic	9	6240	2.5	1375	28300
7 ≤ pH	Mineral	74	86	7.4	3	2305
	Organic	2	3100 ^a	—	—	—

^aPopulation was not fitted due to the low number of entries

recognised and values are highly variable. For uranium, F_v values cited in IAEA (2010) range over more than five orders of magnitude. However, in general uranium is bioexcluded from plants rather than bioaccumulated. Recommended geometric mean and geometric standard deviation values for different types of plants and different plant parts are listed in Table 2, together with the minimum and maximum values recorded. Where possible, distinctions between different soil types are also made.

This data set was used by Vandenhove et al. (2009) to analyse differences between crop groups. They reported that fodder, pasture and herbs had the highest values (2.3×10^{-2} to 6.5×10^{-2}), with legumes, tuber and cereals the lowest values (2.2×10^{-3} to 6.5×10^{-3}) and that differences were significant ($p < 0.05$). Data within crop groups were variable with a range of two or three orders of magnitude being common. The authors concluded that experimental conditions, climate, soil parameters (pH, cation exchange capacity, organic matter or clay content, amorphous Fe) and contamination event did not significantly affect transfer factors.

Relatively extensive data for F_v values are also available for tropical environments (IAEA 2010; Saeed et al. 2011; Kritsananuwat et al. 2015), and data are also available for sub-tropical regions (Jazzar and Thabayneh 2014; Skoko et al. 2014) and for forests in Finland (Rovainen et al. 2011), Norway (Popic et al. 2011) and Southern India (Manigandan and Shekar 2014).

In general, uranium tends to accumulate in the roots of plants rather than above-ground parts (Kohler et al. 2000; Chen et al. 2005; Laroche et al. 2005; Pulhani et al. 2005; Al-Kharouf et al. 2008; Shtangeeva 2010; Soudek et al. 2014). Also, there is contradictory evidence as to whether the accumulation of uranium increases with the age of the plant or plant part (Sheppard and Evenden 1988; Saric et al. 1995; Soudek et al. 2014).

Table 2 Temperate environment soil-plant transfer factors, F_v , for uranium (IAEA 2010)

Plant group	Plant compartment	Soil group	Number of samples	Geometric mean	Geometric standard deviation	Minimum	Maximum
All		All	781	2.3×10^{-2}	9.1	3.0×10^{-5}	1.3×10^1
Cereals	Grain	All	59	6.2×10^{-3}	7.7	1.6×10^{-4}	8.2×10^{-1}
		Sand	6	8.9×10^{-3}	1.1×10^1	1.9×10^{-4}	6.2×10^{-2}
		Loam	20	7.7×10^{-3}	5.1	1.6×10^{-4}	6.2×10^{-2}
		Clay	11	3.8×10^{-3}	4.0	7.6×10^{-4}	5.0×10^{-2}
	Stems and shoots	All	55	2.7×10^{-2}	7.5	3.0×10^{-5}	3.5
		Sand	6	3.4×10^{-2}	6.0	2.1×10^{-3}	1.7×10^{-1}
		Loam	25	5.4×10^{-2}	6.30	7.4×10^{-4}	3.5
		Clay	8	1.0×10^{-2}	3.6	2.8×10^{-3}	9.8×10^{-2}
Maize	Grain	All	9	1.5×10^{-2}	1.2×10^1	5.0×10^{-4}	7.1×10^{-1}
	Stems and shoots	All	11	7.8×10^{-3}	1.4×10^1	1.6×10^{-4}	9.6×10^{-1}
Leafy vegetables	Leaves	All	108	2.0×10^{-2}	7.3	7.8×10^{-5}	8.8
		Sand	7	1.7×10^{-1}	1.5×10^1	1.5×10^{-3}	8.8
		Loam	14	4.3×10^{-2}	3.9	7.7×10^{-3}	2.7×10^{-1}
		Clay	9	3.6×10^{-3}	4.2	7.6×10^{-4}	4.3×10^{-2}
		Organic	6	1.8×10^{-1}	9.7	7.9×10^{-3}	8.0
Non-leafy vegetables	Fruits, heads, berries, buds	All	38	1.5×10^{-2}	4.2	5.2×10^{-4}	2.0×10^{-1}
		Sand	7	1.9×10^{-2}	5.5	1.3×10^{-3}	1.6×10^{-1}
		Loam	4	2.3×10^{-2}	2.2	7.6×10^{-3}	4.7×10^{-2}
		Clay	7	1.8×10^{-2}	4.2	5.0×10^{-3}	2.0×10^{-1}
	Stems and shoots	All	6	5.3×10^{-2}	9.9	4.3×10^{-3}	7.1×10^{-1}
Leguminous vegetables	Seeds and pods	All	19	2.2×10^{-3}	1.2×10^1	5.4×10^{-5}	1.5×10^{-1}
		Loam	4	3.0×10^{-3}	1.8×10^1	5.4×10^{-5}	4.7×10^{-2}
		Clay	7	5.5×10^{-4}	4.7	5.7×10^{-5}	5.0×10^{-3}
	Stems and shoots	All	21	6.4×10^{-2}	1.4×10^1	7.4×10^{-4}	8.7
		Sand	6	2.8×10^{-1}	2.0×10^1	5.3×10^{-3}	8.7
		Loam	6	1.2×10^{-2}	6.2	7.4×10^{-4}	1.4×10^{-1}
Root crops	Roots	All	46	8.4×10^{-3}	6.2	4.9×10^{-4}	2.6×10^{-1}
		Sand	9	7.8×10^{-3}	5.9	9.9×10^{-4}	2.3×10^{-1}
		Loam	10	2.5×10^{-2}	3.2	2.6×10^{-3}	1.2×10^{-1}
		Clay	5	6.8×10^{-3}	6.2	7.9×10^{-4}	9.2×10^{-2}
	Stems and shoots	All	37	2.8×10^{-2}	5.4	2.0×10^{-3}	7.0×10^{-1}
		Sand	9	2.5×10^{-2}	5.6	2.0×10^{-3}	2.4×10^{-1}
		Loam	11	5.0×10^{-2}	3.0	1.3×10^{-2}	3.2×10^{-1}
		Clay	5	1.1×10^{-2}	4.3	2.0×10^{-3}	5.8×10^{-2}

(continued)

Table 2 (continued)

Plant group	Plant compartment	Soil group	Number of samples	Geometric mean	Geometric standard deviation	Minimum	Maximum
Tubers	Tubers	All	28	5.0×10^{-3}	6.4	1.8×10^{-4}	8.0×10^{-2}
		Sand	4	1.9×10^{-2}	3.8	4.3×10^{-3}	7.8×10^{-2}
		Loam	3	2.8×10^{-2}	3.2	8.2×10^{-3}	8.0×10^{-2}
		Clay	6	9.2×10^{-4}	3.0	1.9×10^{-4}	4.8×10^{-3}
	Stems and shoots	All	1	1.9×10^{-1}			
Herbs		All	9	3.6×10^{-2}	4.9	8.6×10^{-3}	4.1×10^{-1}
Other crops	Leaves (sunflower)	All	39	7.1×10^{-2}	3.9	8.9×10^{-3}	7.8
		Sand	5	4.1×10^{-1}	5.3	1.6×10^{-1}	7.8
		Loam	22	7.1×10^{-2}	2.9	1.0×10^{-2}	6.4×10^{-1}
		Clay	11	2.7×10^{-2}	2.1	8.9×10^{-3}	1.0×10^{-1}
	Grain (sunflower)	All	2	1.5×10^{-2}		8.2×10^{-3}	2.9×10^{-2}
Grasses	Stems and shoots	All	147	1.7×10^{-2}	9.4	2.0×10^{-4}	5.5
		Sand	19	1.6×10^{-2}	1.7×10^1	5.5×10^{-4}	1.8
		Loam	34	9.8×10^{-3}	8.4	3.1×10^{-4}	4.6×10^{-1}
Pasture	Stems and shoots	All	53	4.6×10^{-2}	5.3	1.3×10^{-3}	1.4×10^1
		Sand	3	2.7×10^{-3}	1.8	1.3×10^{-3}	3.9×10^{-3}
		Loam	7	7.2×10^{-2}	3.3×10^1	1.8×10^{-3}	1.4×10^1
Leguminous fodder	Stems and shoots	All	15	1.5×10^{-2}	4.2	2.0×10^{-3}	1.6
		Sand	12	1.0×10^{-2}	2.0	2.0×10^{-3}	2.1×10^{-2}

2.4 Transfers of Uranium to Terrestrial Animals

Both the IAEA (2010) and Thorne (2003) have reviewed transfer factors between the diet of animals and various food products. These transfer factors are ratios of the concentration in the food product for chronic exposure to the rate of intake in the diet. Transfer factors to milk are generally $2 \text{ } 10^{-3} \text{ d L}^{-1}$ or lower, and transfer factors to beef are less than $1 \text{ } 10^{-3} \text{ d kg}^{-1}$. Values for pork are typically rather larger (between $1 \text{ } 10^{-3}$ and $1 \text{ } 10^{-2} \text{ d kg}^{-1}$). For poultry meat and eggs values of about 1 d kg^{-1} are recorded. These results are broadly as would be expected if uranium uptake and retention is independent of the mass of the animal, because this results in transfer factors that vary in inverse proportion to body mass.

Thorne (2003) also analysed kinetic data on the retention of uranium in animals and demonstrated that these data are broadly consistent with the transfer factors given above, except that gastrointestinal absorption may be enhanced in poultry compared with the other types of animal studied.

The IAEA (2014) has provided concentration ratios for wildlife relative to the environmental media that comprise their habitats. These data are set out in Table 3.

Table 3 Concentration ratios for uranium in wildlife in various types of ecosystem (IAEA 2014)

Wildlife group: terrestrial	Concentration ratio (Bq per kg fresh weight whole organism/Bq per kg dry weight soil)						
	AM	AMSD	GM	GMSD	Minimum	Maximum	N
Annelids	$8.8 \cdot 10^{-3}$						1
Arthropods	$1.8 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	$1.3 \cdot 10^0$	$1.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	4
Birds: herbivorous	$5.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$4.9 \cdot 10^{-4}$	$1.3 \cdot 10^0$	$4.1 \cdot 10^{-4}$	$6.8 \cdot 10^{-4}$	20
Grasses and herbs	$1.4 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$	$4.5 \cdot 10^{-2}$	$4.6 \cdot 10^0$	$7.7 \cdot 10^{-5}$	$5.5 \cdot 10^0$	439
Grasses	$1.3 \cdot 10^{-1}$	$4.0 \cdot 10^{-1}$	$3.7 \cdot 10^{-2}$	$4.8 \cdot 10^0$	$7.7 \cdot 10^{-5}$	$5.5 \cdot 10^0$	280
Herbs	$2.1 \cdot 10^{-1}$	$5.5 \cdot 10^{-1}$	$7.6 \cdot 10^{-2}$	$4.2 \cdot 10^0$	$2.2 \cdot 10^{-3}$	$2.8 \cdot 10^0$	64
Lichens and bryophytes	$2.5 \cdot 10^0$	$4.4 \cdot 10^0$	$1.3 \cdot 10^0$	$3.2 \cdot 10^0$	$2.0 \cdot 10^{-2}$	$2.9 \cdot 10^1$	237
Mammals	$5.8 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$2.5 \cdot 10^0$	$1.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-2}$	22
Mammals: marsupial	$6.2 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$2.6 \cdot 10^0$	$8.0 \cdot 10^{-4}$	$2.1 \cdot 10^{-2}$	12
Reptiles	$1.5 \cdot 10^0$	$3.1 \cdot 10^0$	$6.7 \cdot 10^{-1}$	$3.6 \cdot 10^0$	$1.3 \cdot 10^{-4}$	$2.5 \cdot 10^0$	21
Shrubs	$2.3 \cdot 10^{-1}$	$6.4 \cdot 10^{-1}$	$8.1 \cdot 10^{-2}$	$4.3 \cdot 10^0$	$1.4 \cdot 10^{-5}$	$5.9 \cdot 10^0$	970
Trees	$6.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$	$2.9 \cdot 10^{-3}$	$3.7 \cdot 10^0$	$1.4 \cdot 10^{-5}$	$3.2 \cdot 10^{-2}$	521
Wildlife group: freshwater	Concentration ratio (Bq per kg fresh weight whole organism/Bq per L of water)						
	AM	AMSD	GM	GMSD	Minimum	Maximum	N
Crustaceans	$2.0 \cdot 10^2$	$3.1 \cdot 10^2$	$1.1 \cdot 10^2$	$3.1 \cdot 10^0$			5
Fish	$3.1 \cdot 10^1$	$1.0 \cdot 10^2$	$9.1 \cdot 10^0$	$4.8 \cdot 10^0$	$5.0 \cdot 10^{-2}$	$7.6 \cdot 10^2$	1294
Fish: benthic feeding	$7.5 \cdot 10^1$	$2.1 \cdot 10^2$	$2.6 \cdot 10^1$	$4.3 \cdot 10^0$	$6.0 \cdot 10^{-1}$	$7.6 \cdot 10^2$	99
Fish: piscivorous	$2.2 \cdot 10^1$	$4.0 \cdot 10^1$	$1.1 \cdot 10^1$	$3.4 \cdot 10^0$	$5.1 \cdot 10^{-1}$	$1.7 \cdot 10^2$	84
Molluscs: bivalve	$5.6 \cdot 10^2$	$1.3 \cdot 10^2$	$5.4 \cdot 10^2$	$1.3 \cdot 10^0$			3
Phytoplankton	$7.1 \cdot 10^1$	$4.7 \cdot 10^1$	$5.9 \cdot 10^1$	$1.8 \cdot 10^0$	$4.0 \cdot 10^1$	$1.8 \cdot 10^2$	40
Reptiles	$1.2 \cdot 10^2$	$9.6 \cdot 10^1$	$9.0 \cdot 10^1$	$2.1 \cdot 10^0$	$4.5 \cdot 10^1$	$1.9 \cdot 10^2$	8
Vascular plants	$3.7 \cdot 10^2$	$9.9 \cdot 10^2$	$1.3 \cdot 10^2$	$4.2 \cdot 10^0$	$2.9 \cdot 10^1$	$2.7 \cdot 10^3$	386

(continued)

Table 3 (continued)

Wildlife group: terrestrial	Concentration ratio (Bq per kg fresh weight whole organism/Bq per kg dry weight soil)						
	AM	AMSD	GM	GMSD	Minimum	Maximum	N
Wildlife group: marine	Concentration ratio (Bq per kg fresh weight whole organism/Bq per L of water)						
	AM	AMSD	GM	GMSD	Minimum	Maximum	N
Fish	$8.8 \cdot 10^0$	$6.1 \cdot 10^0$	$7.3 \cdot 10^0$	$1.9 \cdot 10^0$	$2.0 \cdot 10^0$	$1.8 \cdot 10^1$	9
Macroalgae	$8.3 \cdot 10^1$	$9.9 \cdot 10^1$	$5.4 \cdot 10^1$	$2.6 \cdot 10^0$	$2.1 \cdot 10^1$	$5.1 \cdot 10^2$	47
Molluscs	$3.2 \cdot 10^1$	$3.0 \cdot 10^1$	$2.4 \cdot 10^1$	$2.2 \cdot 10^0$	$4.0 \cdot 10^0$	$9.7 \cdot 10^1$	22
Molluscs: bivalve	$3.5 \cdot 10^1$	$3.5 \cdot 10^1$	$2.5 \cdot 10^1$	$2.3 \cdot 10^0$	$4.0 \cdot 10^0$	$9.7 \cdot 10^1$	13
Phytoplankton	$2.2 \cdot 10^2$	$2.3 \cdot 10^2$	$1.5 \cdot 10^2$	$2.4 \cdot 10^0$	$1.0 \cdot 10^1$	$6.0 \cdot 10^2$	10
Sea anemones, true corals	$9.9 \cdot 10^2$	$4.4 \cdot 10^2$	$9.1 \cdot 10^2$	$1.5 \cdot 10^0$	$4.2 \cdot 10^2$	$1.8 \cdot 10^3$	38
Vascular plants	$2.4 \cdot 10^2$				$1.7 \cdot 10^2$	$3.0 \cdot 10^2$	2
Zooplankton	$3.7 \cdot 10^0$	$4.8 \cdot 10^0$	$2.3 \cdot 10^0$	$2.7 \cdot 10^0$	$1.7 \cdot 10^{-1}$	$5.5 \cdot 10^0$	3
Wildlife group: brackish	Concentration ratio (Bq per kg fresh weight whole organism/Bq per L of water)						
	AM	AMSD	GM	GMSD	Minimum	Maximum	N
Crustaceans	$3.5 \cdot 10^0$	$2.3 \cdot 10^0$	$3.0 \cdot 10^0$	$1.8 \cdot 10^0$	$8.3 \cdot 10^{-1}$	$7.6 \cdot 10^0$	9
Fish	$4.6 \cdot 10^{-1}$	$1.7 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$	$1.4 \cdot 10^0$	$4.0 \cdot 10^{-1}$	$5.6 \cdot 10^{-1}$	9
Macroalgae	$3.9 \cdot 10^1$	$7.8 \cdot 10^1$	$1.7 \cdot 10^1$	$3.6 \cdot 10^0$	$8.6 \cdot 10^{-1}$	$3.3 \cdot 10^2$	49
Molluscs	$2.6 \cdot 10^1$	$2.5 \cdot 10^1$	$1.9 \cdot 10^1$	$2.2 \cdot 10^0$	$3.7 \cdot 10^0$	$9.1 \cdot 10^1$	27
Vascular plants	$1.4 \cdot 10^2$	$4.6 \cdot 10^1$	$1.3 \cdot 10^2$	$1.4 \cdot 10^0$			3

AM arithmetic mean, AMSD arithmetic mean standard deviation, GM geometric mean, GMSD geometric mean standard deviation, N number of data

Although of limited relevance in assessment studies, it is worth noting that there has been some interest in the use of earthworms as biomarkers for uranium. Bioaccumulation tends to be greater at lower concentrations of uranium in soil, suggesting adaptation of the organisms by enhanced bioexclusion (Di Leila et al. 2005; Giovanetti et al. 2010). Observed effects included histological changes in the body wall and gastrointestinal tract, and it has been suggested that such histopathological changes could be a useful biomarker of soil quality (Lourenço et al. 2011, 2012).

2.5 *Interactions with Freshwater Sediments and Uptake by Freshwater Biota*

Freshwater sediments often serve as a sink for uranium, with uranium partitioning between sediments and water affected by pH, hardness, alkalinity (as bicarbonate), redox potential, dissolved organic matter concentration, phosphorus concentration, presence of complexing agents and sediment particle size and mineral composition (Allard et al. 1979, 1982; Brunskill and Wilkinson 1987; Herczeg et al. 1988; Premuzic et al. 1995; Markich 2002; USGS 2008; Goulet et al. 2012; ATSDR 2013). Reported distribution coefficients range from 9 to 15,000 L kg⁻¹ (IAEA 2018).

The factors that affect the partitioning of uranium between freshwater sediments and water also affect the bioavailability of the element. An important consideration is competition with calcium and magnesium for uptake. In addition, at high pH the complexation of uranium with carbonates may reduce its bioavailability. Uptake by biota may occur both by ingestion of food and sediment and by passive diffusion through the gills (Langston and Spence 1995; Rand et al. 1995; Köster 2004; Marsden and Rainbow 2004; Goulet et al. 2012). However, the assimilation efficiency from the gastrointestinal tract is likely to be low (Simon and Garnier-Laplace 2005), and it seems likely that uranium is primarily taken up via the gills (Goulet et al. 2012). Typical transfer factors for freshwater biota are 100 to 1000 for algae and plankton, and for freshwater invertebrates, but are about 1 to 30 for freshwater fish (IAEA 2009, 2010, 2014).

2.6 *Interactions with Marine Sediments and Uptake by Marine Biota*

Uranium can enter estuarine, coastal and marine systems either directly in groundwater or in freshwater discharges. Rather limited data are available on K_d values for uranium in marine sediments. The IAEA (2004) provide reference values based on exchange with carbonates in the sediments. These values are expressed as the ratio of Bq kg⁻¹ sediment to Bq kg⁻¹ seawater, i.e. as dimensionless values. However, it is more usual to give values expressed as Bq kg⁻¹ sediment to Bq per m³ of seawater, i.e. with units of m³ kg⁻¹. This convention is adopted here. The reference values are 0.5 m³ kg⁻¹ for deep ocean sediments (with a reported range from 0.1 to 5 m³ kg⁻¹) and 1.0 m³ kg⁻¹ for ocean margin sediments (with reported values of 1.0 and 5 to 10 m³ kg⁻¹).

The distribution of dissolved uranium in sea water is very similar across marine systems, and a concentration of 3.3 µg L⁻¹ of ²³⁸U is a reasonable average in sea water from coastal environments as well as the deep sea.

As in freshwater systems, absorption of uranium by organisms occurs to a small extent, and there are no identified cases of uranium buildup in food chains. Concentration ratio values have been reviewed and compiled by the IAEA (2004).

Table 4 Recommended concentration ratios for uranium in marine biota (IAEA 2004)

Biota	Recommended concentration ratio	Comments
Fish	1.0	Previously, a value of 0.1 was recommended (IAEA 1978). Typical concentrations of uranium in fish flesh of about $0.2 \mu\text{g kg}^{-1}$ wet weight are reported in the literature (Pentreath 1977). The concentration ratio derived using this concentration is less than 0.1 but was increased to 1.0 to allow for the possible inclusion of some bone in the edible fraction
Crustaceans	10	As previously given in IAEA (1978)
Molluscs (excluding cephalopods)	30	Reported data give ^{238}U concentrations of 3.0, 5.5, 4.6 and 13 Bq kg^{-1} dry weights for four different lamellibranch molluscs, giving a mean concentration of 1.2 Bq kg^{-1} wet weight (Hodge et al. 1979). The recommended concentration ratio was derived using this concentration and is consistent with the mean concentration ratio reported by Swift and Kershaw (1999)
Macroalgae	100	Previously, a value of 10 was recommended (IAEA 1978). The data reported by Holm and Persson (1980) for brackish water and Nilsson et al. (1981) give a dry weight concentration ratio of 700 for uranium in brown algae. However, ^{238}U determinations for <i>Macrocystis</i> , another brown alga, gave an average concentration of 7.2 Bq kg^{-1} dry weight (Hodge et al. 1979), indicating a concentration ratio of about 35. A value of 1×10^2 is recommended, but the IAEA (2004) comments that this may well be too high
Zooplankton	30	Derived using data from Ballestra and Noshkin (1991)
Phytoplankton	20	Derived using data from Szefer and Ostrowski (1980)

Table 3, based on IAEA (2014), gives a summary of uranium concentration factors for various groups of biota from brackish and marine environments, and Table 4 gives recommended concentration ratio values from IAEA (2004).

3 Assessing Radiological and Toxicological Impacts when Environmental Concentrations Are Known

3.1 Radiotoxicity to Humans

The radiotoxicity of uranium to humans is expressed in terms of the committed effective dose received per unit intake of activity. Values of committed effective dose per unit intake are calculated using biokinetic models developed on behalf of the ICRP (1994, 1995, 1996) and are compiled in ICRP (2012). Values appropriate

to members of the public are listed in Table 5. This table includes both uranium radioisotopes and their progeny, as data for the progeny are required when estimating the radiotoxicity of uranium in which progeny are present (either because natural uranium is under consideration or because in-growth has occurred in uranium after its separation). For inhalation, the values are given for aerosols exhibiting fast, medium or slow rates of clearance from the respiratory system [see ICRP 1994 for details of how these different clearance classes are modelled]. In practice, compounds of uranium often exhibit clearance characteristics that are intermediate between these classes (Leggett and Meck 2018).

To make comparisons between the chemical toxicity and radiotoxicity of uranium, it is often useful to give values of committed effective dose per unit mass of ingested or inhaled uranium. These values depend upon whether the uranium is depleted, natural or enriched, as well as the degree to which radioactive progeny are present, and the physical and chemical form of the uranium. Thorne and Wilson (2015) provide a tabulation of such values, and this is reproduced, in part, in Table 6.

Table 5 Values of committed effective dose per unit intake (Sv Bq^{-1}) for uranium and its progeny and for adult members of the public (ICRP 2012)

Radionuclide	Branching ratio	Effective dose per unit intake for adult members of the public (Sv Bq^{-1})			
		Inhalation of type F	Inhalation of type M	Inhalation of type S	Ingestion
U-238	1.00	5.00E-07	2.90E-06	8.00E-06	4.50E-08
Th-234	1.00	2.50E-09	6.60E-09	7.70E-09	3.40E-09
Pa-234	1.00		3.80E-10	4.00E-10	5.10E-10
U-234	1.00	5.60E-07	3.50E-06	9.40E-06	4.90E-08
Th-230	1.00	1.00E-04	4.30E-05	1.40E-05	2.10E-07
Ra-226	1.00	3.60E-07	3.50E-06	9.50E-06	2.80E-07
Pb-214	1.00	2.80E-09	1.40E-08	1.50E-08	1.40E-10
Bi-214	1.00	7.10E-09	1.40E-08		1.10E-10
Pb-210	1.00	9.00E-07	1.10E-06	5.60E-06	6.90E-07
Bi-210	1.00	1.10E-09	9.30E-08		1.30E-09
Po-210	1.00	6.10E-07	3.30E-06	4.30E-06	1.20E-06
U-235	1.00	5.20E-07	3.10E-06	8.50E-06	4.70E-08
Th-231	1.00	7.80E-11	3.10E-10	3.30E-10	3.40E-10
Pa-231	1.00		1.40E-04	3.40E-05	7.10E-07
Ac-227	1.00	5.50E-04	2.20E-04	7.20E-05	1.10E-06
Th-227	0.99	6.70E-07	8.50E-06	1.00E-05	8.80E-09
Fr-223	0.01	8.90E-10			2.40E-09
Ra-223	1.00	1.20E-07	7.40E-06	8.70E-06	1.00E-07
Pb-211	1.00	3.90E-09	1.10E-08	1.20E-08	1.80E-10

Types F (fast), M (medium) and S (slow) relate to different rates of solubilisation of aerosols in the respiratory system. Branching yields are expressed as fractional yields, i.e. Ac-227 decays either to Th-227 or Fr-233, but both then decay to Ra-223

Table 6 Values of committed effective dose per unit mass intake of various forms of uranium for adult members of the public (Thorne and Wilson 2015)

Material	Committed effective dose per unit mass intake (Sv mg ⁻¹)			
	Adult members of the public			
	Type F	Type M	Type S	Ingestion
Natural: no progeny	1.34E-05	8.06E-05	2.19E-04	1.23E-06
Natural: progeny in equilibrium	1.66E-03	9.24E-04	7.03E-04	3.16E-05
Depleted uranium	1.33E-05	7.99E-05	2.17E-04	1.22E-06
1 percent enriched: no ²³⁴ U enrichment	1.35E-05	8.13E-05	2.21E-04	1.24E-06
1 percent enriched: ²³⁴ U enrichment	1.71E-05	1.04E-04	2.81E-04	1.56E-06
2 percent enriched: no ²³⁴ U enrichment	1.38E-05	8.31E-05	2.26E-04	1.27E-06
2 percent enriched: ²³⁴ U enrichment	3.03E-05	1.84E-04	5.02E-04	2.71E-06
3 percent enriched: no ²³⁴ U enrichment	1.41E-05	8.50E-05	2.31E-04	1.30E-06
3 percent enriched: ²³⁴ U enrichment	4.34E-05	2.68E-04	7.23E-04	3.86E-06
4 percent enriched: no ²³⁴ U enrichment	1.43E-05	8.62E-05	2.34E-04	1.32E-06
4 percent enriched: ²³⁴ U enrichment	5.65E-05	3.50E-04	9.43E-04	5.01E-06
5 percent enriched: no ²³⁴ U enrichment	1.46E-05	8.80E-05	2.39E-04	1.34E-06
5 percent enriched: ²³⁴ U enrichment	6.96E-05	4.32E-04	1.16E-03	6.16E-06
20 percent enriched: ²³⁴ U enrichment	1.94E-04	1.21E-03	3.24E-03	1.70E-05
90 percent enriched: ²³⁴ U enrichment	1.33E-03	8.31E-03	2.23E-02	1.17E-04

For depleted uranium, the calculations assume that ²³⁴U is in secular equilibrium with ²³⁸U. If ²³⁴U is depleted to any significant degree, the values of committed effective dose per unit mass intake will be somewhat decreased. Enrichment of uranium typically uses techniques that are based on isotopic mass differences. These enrich ²³⁴U more than ²³⁵U. However, laser enrichment is specific to ²³⁵U and does not enrich ²³⁴U.

3.2 Chemical Toxicity to Humans

For all but the most insoluble forms of uranium, damage to the kidneys is the adverse chemical effect of greatest concern (Leggett 1989; ATSDR 2013). Two alternative approaches to assessing the chemical toxicity of intakes of uranium have been adopted. In ATSDR (2013), no-observed-adverse-effect levels (NOAELs) or lowest-observed-adverse-effect levels (LOAELs) are established for inhalation and ingestion exposures. Uncertainty factors (see Table 7) are then applied to set minimal risk levels (MRLs) for human exposure. Table 7 summarises the MRLs recommended by ATSDR (2013). This topic is discussed further in Wilson and Thorne (2015).

In Table 7, the benchmark dose level (BMDL) is defined by ATSDR (2013) to be a concentration or intake rate that produces a predetermined change in the response rate of an adverse effect in an organism compared with background. Thus, a BMDL₁₀ represents a 10% change in response rate. Acute, intermediate and chronic exposure durations are 14 days or less, 14–365 days and more than 365 days, respectively. Note that MRL values for ingestion are expressed per unit of body mass. Thus, they imply different limits on total intake rates for infants, children and adults.

Table 7 Minimal risk levels for uranium [based on ATSDR 2013]

Route	Form	Duration	MRL	Basis	Uncertainty factor
Inhaled	Soluble	Intermediate	1×10^{-4} mg [U] m ⁻³	LOAEL of 0.15 mg [U] m ⁻³ for minimal renal lesions in dogs. Adjusted for intermittent exposure resulting in an adjusted LOAEL of 0.032 mg [U] m ⁻³	300
		Chronic	4×10^{-5} mg[U] m ⁻³	One-year dog study involving exposure to UCl ₄ . A BMCL ₁₀ of 0.019 mg [U] m ⁻³ was selected. This BMCL ₁₀ was adjusted for intermittent exposure resulting in an adjusted BMCL ₁₀ of 0.0037 mg [U] m ⁻³	100
Insoluble	Intermediate	Intermediate	2×10^{-3} mg [U] m ⁻³	A NOAEL of 1.1 mg [U] m ⁻³ in dogs was used (based on renal effects). This value was adjusted for intermittent exposure resulting in an adjusted NOAEL of 0.24 mg [U] m ⁻³	100
		Chronic	8×10^{-4} mg[U] m ⁻³	A LOAEL of 5.1 mg [U] m ⁻³ for lung fibrosis and metaplasia in rhesus monkeys was selected. This LOAEL was adjusted for intermittent exposure resulting in an adjusted LOAEL of 0.82 mg [U] m ⁻³	1000

(continued)

Table 7 (continued)

Route	Form	Duration	MRL	Basis	Uncertainty factor
Ingested	Soluble	Acute	$2 \times 10^{-3} \text{ mg [U] kg}^{-1} \text{ d}^{-1}$	A BMDL ₀₅ value of 0.20 mg [U] kg ⁻¹ d ⁻¹ for cleft palate in mice was selected; this is lower than the BMDL ₀₅ values for other foetal effects in mice and is approximately tenfold lower than the LOAEL for maternal and foetal body weight effects. Thus, it is likely to be protective of the other effects	100
	Intermediate		$2 \times 10^{-4} \text{ mg [U] kg}^{-1} \text{ d}^{-1}$	Statistically significant increases in renal lesions in rats, LOAEL value of 0.06 mg [U] kg ⁻¹ d ⁻¹	300
	Chronic		$2 \times 10^{-4} \text{ mg [U] kg}^{-1} \text{ d}^{-1}$	Given the ability of the kidney to repair renal damage at low exposure levels, the intermediate-duration oral MRL was taken as protective for chronic exposures	Not applicable

In the second approach, a limit is set based on the maximum acceptable kidney concentration, and a biokinetic model is used to relate this maximum concentration to an intake rate by ingestion or inhalation that would give rise to that concentration. The maximum kidney concentration that is likely to be without an appreciable risk of adverse non-cancer effects has been discussed by Leggett (1989), and an updated evaluation is given by Wilson and Thorne (2015).

Animal studies during the 1940s suggested that up to 2–3 µg [U] g⁻¹ of the kidney might be accumulated without serious effects and in 1959 a limiting concentration of 3 µg [U] g⁻¹ of the kidney was adopted by the ICRP.

Subsequently, Stopps and Todd (1982) commented that although 2–3 µg [U] g⁻¹ of the kidney might be tolerated without the occurrence of serious tissue damage, renal abnormalities and mild renal injuries could occur at concentrations of as low as 0.1–0.4 µg [U] g⁻¹ of the kidney. Following on from this work, Leggett (1989) concluded that the kidney may develop a kind of acquired tolerance to uranium after

repeated exposures, but the kidney that has developed such a tolerance is not normal. Thus, tolerant animals have high urine volumes, a diminished glomerular filtration rate and a loss of concentrating capacity by the kidney. In his view, the concentration of $3 \mu\text{g [U] g}^{-1}$ of kidney applied for many years as a guidance level for limiting occupational exposures was based on tests of chemical toxicity that were less sensitive and on definitions of chemical toxicity that were less stringent, than those developed subsequently. Moreover, in the underpinning human studies, the subjects may have been exposed to kidney concentrations in the order of $3 \mu\text{g [U] g}^{-1}$ of kidney only for very brief periods. Leggett (1989) concluded that it might be prudent to lower this long-standing guidance level by roughly an order of magnitude.

More recently, the WHO (2012) has set the tolerable daily intake (TDI) of uranium as $60 \mu\text{g}$, based on an epidemiological study by Kurtio et al. (2006) that was used to define a no-effect group. The value of the 95th percentile of the uranium exposure distribution for this group was estimated to be $1094 \mu\text{g d}^{-1}$ (95% confidence interval on the 95th percentile was $637\text{--}1646 \mu\text{g d}^{-1}$). The TDI was taken to be 10% of the lower bound of the 95% confidence interval on the 95th percentile of the exposure distribution for this group. For comparison, ATSDR (2013) has recommended a MRL value for chronic exposure to uranium by ingestion of $0.2 \mu\text{g kg}^{-1} \text{d}^{-1}$. For a reference adult of mass 70 kg (ICRP 1975), this corresponds to $14 \mu\text{g d}^{-1}$. Given the very different bases of derivation, the relatively small difference between the TDI and MRL values suggests that a robust basis exists for limiting intakes of uranium by ingestion.

To interpret the WHO TDI in terms of the equivalent kidney concentration, it is necessary to establish the relationship between the chronic intake rate of uranium and the maintained kidney concentration that is achieved at equilibrium. Wilson and Thorne (2015) have shown that an ingestion intake rate of $1 \mu\text{g [U] d}^{-1}$ by adults corresponds to a maintained kidney concentration of $2.2 \times 10^{-4} \mu\text{g [U] g}^{-1}$ of the kidney. Thus, the TDI corresponds to $0.013 \mu\text{g [U] g}^{-1}$ of kidney. This is well below the value of $0.3 \mu\text{g [U] g}^{-1}$ of kidney that Leggett (1989) considered prudent.

Following from the TDI of $60 \mu\text{g}$ and based on a water consumption rate of 2 L d^{-1} , the WHO (2012) set a provisional guideline value for uranium in drinking water of $30 \mu\text{g [U] L}^{-1}$. This may be compared with the value of $20 \mu\text{g [U] L}^{-1}$ adopted in Australia (Jones et al. 2006), and $30 \mu\text{g [U] L}^{-1}$ in the USA (EPA 2005). To date, no European statutory limits have been imposed for uranium in drinking water. However, European Directive 98/83/EC stipulates that waters in which alpha-emitter concentrations exceed 0.1 Bq L^{-1} should be investigated to determine what corrective action, if any, is required. For natural uranium present without any progeny, 0.1 Bq L^{-1} corresponds to $4 \mu\text{g [U] L}^{-1}$, which is a more stringent restriction than the values recommended preventing chemotoxic effects.

3.3 Radiological Toxicity to Biota

For assessing radiological impacts on biota, the ICRP adopts a limited number of RAPs and recommends standard concentration ratios for those RAPs relative to the environmental media to which they are exposed. These concentration ratios are listed in Table 8.

The significance of absorbed dose rates to the whole body assessed using these concentration ratios can be determined by comparing them with the derived consideration reference levels (DCRLs) recommended by the ICRP (2014). The ICRP defines a DCRL as a band of dose rate within which there is some chance of a deleterious effect from ionising radiation occurring to individuals of that type of RAP that, when considered together with other relevant information, can be used as a point of reference to optimise the level of effort expended on environmental protection, dependent upon the overall management objectives and the relevant exposure situation (ICRP 2008). The DCRLs adopted by the ICRP (2014) are illustrated in Fig. 2.

3.4 Chemical Toxicity to Biota

In assessing whether specific types of biota or aspects of the environment such as habitat characteristics or biodiversity would be adversely affected by the presence of enhanced concentrations of uranium, reference is appropriately made to environmental quality standards (EQSs). For example, the Canadian Water Quality Guidelines for the Protection of Aquatic Life specify total recoverable freshwater

Table 8 Standard concentration ratios for uranium in reference animals and plants (ICRP 2009)

Terrestrial organism	Concentration ratio (Bq kg ⁻¹ fresh weight/ Bq kg ⁻¹ dry soil)	Aquatic organism (environment)	Concentration ratio (Bq per kg fresh weight/ Bq L ⁻¹ of water)
Bee	1.7 10 ^{-2a}	Trout (freshwater)	8.5 10 ⁰
Earthworm	8.8 10 ⁻³	Frog (freshwater)	9.1 10 ^{0b}
Wild grass	4.3 10 ⁻²	Duck (freshwater)	1.3 10 ^{1c}
Pine tree	9.9 10 ⁻⁴		
Rat	6.5 10 ⁻⁴	Flatfish (marine)	4.0 10 ^{0a}
Deer	3.7 10 ^{-3a}	Crab (marine)	6.2 10 ^{0d}
Duck	4.9 10 ^{-4a}	Brown seaweed (marine)	2.9 10 ¹
Frog	6.7 10 ^{-1b}		

^aValue for the generic wildlife group within which the reference animal or plant fits

^bValue derived from a related reference animal or related generic wildlife group

^cValue obtained using an allometric relationship or other modelling approach

^dValue for the generic wildlife group within which the reference animal or plant fits for the estuarine environment

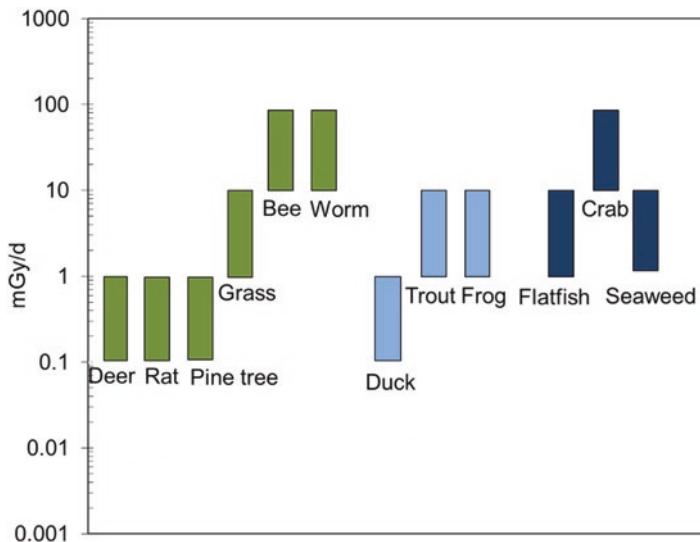


Fig. 2 Derived consideration reference levels adopted by the ICRP (2014)

guideline concentrations of $15 \mu\text{g L}^{-1}$ for long-term exposure and $33 \mu\text{g L}^{-1}$ for short-term exposure (CCME 2011). These values were based on distributions of LC₅₀ values for ten or more species, taking the fifth percentile of the fitted distribution of these values. Similarly, soil quality guidelines for soil contact (SQG_{SC} values) are available for Canada (CCME 2007). These are based on toxicological data for vascular plants and soil invertebrates. A total of 7 studies were selected as acceptable for use, including 15 plant species and 4 invertebrate species. From these studies, a total of 82 acceptable no observable effect concentrations (NOECs), lowest observable effect concentrations (LOECs) and EC₂₀ values were used. EC₂₀ is the effective concentration at which 20% of the exposed population is affected. The 25th percentile of the data distribution was calculated to be 500 mg kg^{-1} and the 50th percentile was 2000 mg kg^{-1} . These then became the environmental soil quality guidelines (SQG_E values) for residential/parkland land use and for commercial and industrial land uses, respectively.

Similarly, the Dutch have defined EQS values for uranium in waters. These values are based on a detailed review and interpretation of the primary literature and consider chemical toxicity only (Van Herwijnen and Verbruggen 2014).

In Australia, a site-specific trigger value for uranium was derived using the framework described in the Australian Water Quality Guidelines and based on eco-toxicological tests using five local test species from four trophic levels (Hogan et al. 2003; Riethmuller et al. 2003).

Within the EU, the implementation of the Water Framework Directive asks for the derivation by member states of environmental protection criteria such as environmental quality standards to allow assessments of the chemical and ecological status of water bodies that should reach a good status from 2015. The transposition

of the Directive into the French legislation led to a regulatory text defining a provisional EQS of $0.3 \mu\text{g L}^{-1}$ for uranium to use in evaluating increments on the natural background (MEDAD 2007).

These examples illustrate that EQSs for uranium have largely been specified by national or regional authorities and have tended to rely on evaluations of the available environmental and toxicological information identified as relevant to the specific situation or range of situations of interest. Generic, international recommendations, as are being developed for radiotoxic substances, have not been developed for uranium as a chemically toxic substance.

Finally, it is noted that Mathews et al. (2009) have presented a method for relating chemical concentrations ($\mu\text{g [U] L}^{-1}$) and dose rates ($\mu\text{Gy h}^{-1}$) for a specific set of reference organisms. This allows a determination as to whether chemical or radiological toxicity is more limiting for depleted, natural, low-enriched and high-enriched uranium in various ecological contexts.

4 Conclusions

Models for representing the transport of radionuclides and other contaminants through both terrestrial and aquatic environments have been developed over several decades, and a mature assessment methodology exists for developing both conceptual and mathematical models that can be applied either generically or in specific environmental contexts (Thorne 2012). Whether simplified 1D models or complex 3D models are employed, there remains substantial reliance on empirically determined parameter values, such as distribution coefficients for soils and sediments, concentration ratios for plants and transfer factors or concentration ratios for animals. For uranium, an extensive database of such information exists. Examination of this database reveals strong dependencies of distribution coefficients on pH and both soil texture and organic matter content. In turn, availability in soil solution can affect plant uptake, but it is generally observed that uranium is bioexcluded from plants rather than being bioaccumulated. The database of information related to transfer factors to terrestrial animals is rather limited, but there is consistency between estimates based on equilibrium and kinetic analyses, and again uranium tends to be bioexcluded rather than bioaccumulated, in part due to limited absorption from the gastrointestinal tract. In terms of biomarkers, earthworms may prove to be a useful organism in which histopathological changes could provide an indication of soil quality.

In freshwaters, the uptake of uranium by sediments is strongly affected by concentrations of calcium and magnesium, and complexation with carbonates at high pH can also be of significance. Uptake is greater in freshwater algae, plankton and invertebrates than it is in freshwater fish. In the latter, uptake is thought to be mainly through the gills. In the marine environment, concentrations of uranium in seawater do not vary very much geographically, and there are no identified cases of uranium buildup in food chains.

In evaluating the effects of uranium on human health and the environment, consideration must be given to both its radiotoxicity and chemotoxicity. For humans, evaluation of radiological impacts can be based on calculations of effective dose and comparisons with ICRP standards. For chemotoxic impacts on humans, nephrotoxicity is the main concern, and direct human experience from both occupational and environmental contexts has been used in standards setting, notably by ATSDR (2013) and WHO (2012). For evaluating radiological impacts on the environment, the ICRP recommends an approach based on RAPs and provides both reference concentration ratios and DCRLs that can be used in assessing the implications of measured or calculated concentrations of uranium in various environmental media. For evaluating chemotoxic impacts on the environment, reliance is mainly placed on EQS values. These have been promulgated by national or regional authorities and have tended to rely on evaluations of the available environmental and toxicological information identified as relevant to the specific situation or range of situations of interest. Generic, international recommendations, as are being developed for radiotoxic substances, have not been developed for uranium as a chemically toxic substance.

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Biokinetic Modelling and Risk Assessment of Uranium in Humans



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Abstract The past few decades have seen substantial experimental and modelling studies addressing the biokinetics of uranium in mammals. Various systemic models have been developed. The degree of absorption of uranium from the gastrointestinal tract is of particular importance and is controlled by the solubility of the uranium compound ingested, previous food consumption and the concomitant administration of oxidizing agents. After entering the plasma, the uranyl ion becomes complexed with bicarbonate, citrate anions and proteins and is dispersed in body tissues. Uranium may then be reabsorbed from various soft tissues, liver, skeleton and kidneys and redeposited or excreted via urine, faeces and hair. The multiple established health effects of uranium ingestion relate to both its chemical and radiological toxicity. Organ-specific and age-adjusted annual effective doses provide insights into possible biomarkers of uranium toxicity in humans. A systematic case study has been carried out in the high-risk-prone area of the Malwa belt of Punjab, India, both estimating the concentrations of uranium in groundwater and evaluating the associated toxicity.

Keywords Uranium biokinetic models · Hazard quotient · Lifetime average daily dose · Age-adjusted dose · Organ-specific dose · Transfer coefficients

1 Background

Uranium is present in almost all rocks, soils, surface waters and groundwater as a mix of three isotopes, ^{238}U (99.2742%), ^{235}U (0.7204%) and ^{234}U (0.0054%), with half-lives of 4.47×10^9 , 7.04×10^8 and 2.46×10^5 years, respectively. In addition, other uranium isotopes (^{236}U and ^{233}U) are released into the environment as a result of various anthropogenic activities, including mining and the production and use of phosphate fertilizers.

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1.1 Presence in Soil

The Earth's surface layers contain, on average, 2.6–2.8 mg kg⁻¹ of uranium (Hu and Gao 2008; Herring 2013). The distribution of this primordial radioactive element is principally dictated by the underlying geology, along with other factors such as pH and mineral composition, as well as thermodynamic parameters, such as temperature and pressure (Chabaux et al. 2003), moisture content and redox potential, and the effects of mineral dissolution and sorption processes (Qafoku et al. 2005; Liu et al. 2009), microbial activity and interactions with the heavy metals present in soils. Concentrations of uranium are controlled by its physical and chemical behaviour and upon processes of diagenesis, such as crystal fractionation in igneous rocks, hydrothermal and metamorphic processes and erosion and depositional mechanisms forming sedimentary rocks. Once deposited, the behaviour of uranium is predominantly governed by ion-exchange mechanisms. Transport of uranium and thorium in soil-water occurs mainly in dissolved or suspended form, by diffusion or mass flow. In soils, uranium is generally found in the +4 and +6 oxidation states.

1.2 Presence in Groundwater

Uranium exists in diverse physicochemical forms, commonly as free metal ions (U^{4+} or UO_2^{2+}) and as complexes with inorganic ligands (like uranyl carbonate at higher pH or uranyl phosphate below $\sim\text{pH } 6.5$) and humic substances (like uranyl fulvate or humate) in dissolved, colloidal and/or particulate forms (Choppin et al. 2002). Primary minerals contain U(IV) as the governing species (Smedley et al. 2006), but in oxidizing media, such as shallow groundwater or surface water, U(VI) dominates. Since hexavalent uranium has greater degree of uptake than its tetravalent counterpart, it is more probable to be a systemic toxicant and forms relatively soluble compounds. Uranium enters groundwater aquifers as a result of natural geochemical processes like mineral dissolution and desorption of adsorbed uranium from mineral surfaces. The concentration of uranium in the aquifer material, the travel time of water through the aquifer, dissolution, adsorption-desorption and recoil processes influence the extent of uranium contamination of groundwater sources (Davidson and Dickson 1986; Tricca et al. 2001). Moreover, factors like ionic and organic content of stream water, chemical constituents of deposited sediments and grain size affect transport of uranium in environmental media.

2 Uranium Exposure to Humans

The natural or artificially introduction of uranium into the environment may result in it entering the human body through inhalation, ingestion or through wounds in the skin with air, water, soil or sediment and food. The uranium may be deposited and retained in the human respiratory tract, the gastrointestinal tract or in various

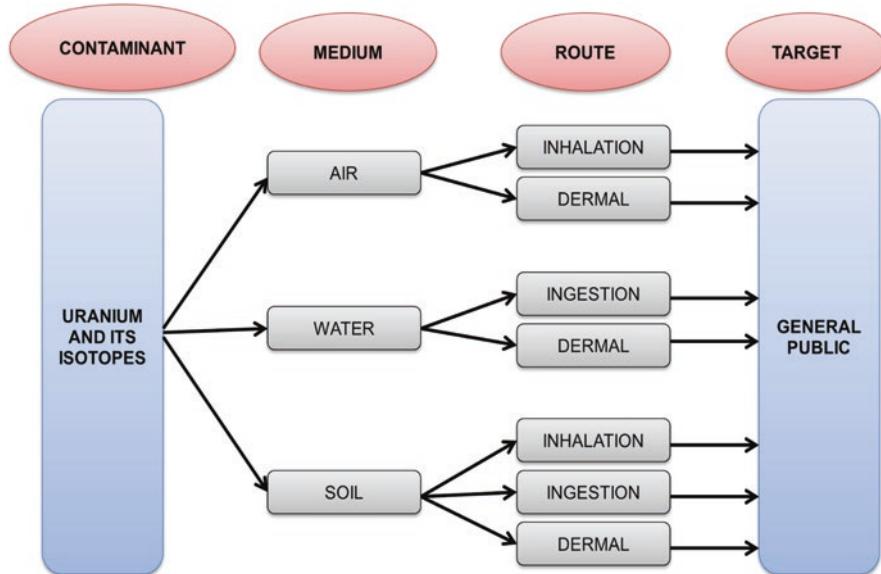


Fig. 1 Pathways of human exposure to environmental contaminants

internal body tissues and organs after transport in various body fluids and blood. The possible pathways of uranium transport from the environment to humans are shown in Fig. 1. Ingestion is normally the dominant route of uranium intake by members of public.

3 Risk Assessment of Uranium Ingestion

Uranium isotopes decay by emission of alpha particles and can contribute substantial radiation doses when present in the body. The health effects of uranium are the combined result of its chemical and radiological toxicity.

3.1 Radiological Toxicity

About 48.9% of the radioactivity of natural uranium is attributed to ^{234}U , 2.2% to ^{235}U and 48.9% to ^{238}U , based on the mass percentages and half-lives of these different uranium isotopes (ATSDR 1999). The radioactivity of uranium poses carcinogenic risks, but the very long half-lives of the dominant uranium isotopes generally make radio toxicity a secondary consideration compared with chemical toxicity (USEPA 2000). The US Environmental Protection Agency proposed the method to assess the radiological risk due to ingestion of uranium in water (USEPA 1999):

$$\text{Cancerrisk} = A_C \times R \quad (1)$$

In the above equation, A_C represents the activity concentration of uranium (Bq L^{-1}). R is the risk factor ($\text{Bq}^{-1} \text{L}$), a product of risk coefficient, r and per capita activity intake, I . Since the specific activity of a radioelement determines its radio toxicity, the choice of risk coefficients depends on the isotopic nature of uranium in water along with its physic-chemical form (Guseva Canu et al. 2011). The cancer mortality risk coefficients (in Bq^{-1}) for the three uranium isotopes ^{234}U , ^{235}U and ^{238}U are 6.1×10^{-11} , 6.2×10^{-11} and 7.5×10^{-11} respectively, whereas cancer morbidity risk coefficients (in Bq^{-1}) are 9.5×10^{-11} , 9.8×10^{-11} and 7.5×10^{-10} , taken in same order.

3.2 Chemical Toxicity

The chemical toxicity of uranium is of relevance only after it enters the body. This toxicity is a function of several environmental parameters. The key ones are carbonate concentration, because of the formation of soluble carbonate complexes, and divalent cation concentration (Ca^{2+} and Mg^{2+}), because of their competitive interactions with the uranyl ion (UO_2^{2+}) (Sheppard et al. 2005). The chemical/noncarcinogenic risk for uranium is quantified in terms of lifetime average daily dose (LADD) and hazard quotient (HQ):

$$\text{LADD} = \frac{\text{EPC} \times \text{IR} \times \text{IF} \times D}{\text{AT} \times W} \quad (2)$$

In the above expression, EPC is the exposure point concentration of uranium in water ($\mu\text{g L}^{-1}$), IR is ingestion rate (taken as 1.4 L day^{-1}), IF is ingestion frequency (365 days y^{-1}), D is duration (taken as a lifetime of 69.89 y), AT is average time (days) and W is the ideal body weight (68.831 kg) (ICRP 2014).

$$\text{HQ} = \frac{\text{LADD}}{\text{RD}} \quad (3)$$

where RD is the reference dose limit taken as $0.6 \mu\text{g kg}^{-1} \text{ day}^{-1}$ (WHO 2004).

3.3 Age-Dependent Annual Ingestion Dose for Different Age Groups

The dose received by a person is dependent on many parameters like:

- (a) The volume or quantity of the contaminant inhaled or ingested
- (b) The fraction of the contaminant reached the respiratory or GI tract

Table 1 Daily water intake for different age groups given by the Institute of Medicine of the National Academies, Washington (2005)

Life stage group	Age	Daily water intake (L d^{-1})
Infants	0–6 months	0.7
	7–12 months	0.8
Children	1–3 y	1.3
	4–8 y	1.7
Males	9–13 y	2.4
	14–18 y	3.3
	>18 y	3.7
Females	9–13 y	2.1
	14–18 y	2.3
	>18 y	2.7
Pregnancy		3.0
Lactation		3.8

- (c) The amount of the contaminant circulated in the body by fluids
- (d) The amount of the contaminant deposited in target tissues or organs

The annual effective ingestion dose, D_a , due to uranium intake via drinking water route is estimated by the following equation:

$$D_a = A_c \times \text{WI} \times \text{DCF} \quad (4)$$

Here, A_c is the activity concentration of uranium in groundwater samples (Bq L^{-1}), WI is the annual water intake (L y^{-1}) and DCF is the dose conversion factor (Sv Bq^{-1}). The assessment of annual ingestion dose must be done separately for different age groups considering the dissimilarities in tissue and organ sensitivity and water consumption. Several factors, such as sex, weight, age and metabolism, determine daily water intake by an individual. The daily water intakes given by the Institute of Medicine of the National Academies, Washington (Institute of Medicine of the National Academies 2005) are listed in Table 1. The daily water intake is generally balanced by losses for maintenance of the total water content in the human body. The dose conversion factors (DCFs) prescribed for infants; children of 1, 5, 10 and 15 years; and adults (>18 years) are 3.4×10^{-7} , 1.2×10^{-7} , 8×10^{-8} , 6.8×10^{-8} , 6.7×10^{-8} and 1.3×10^{-8} Sv Bq^{-1} , respectively (Li et al. 2009; ICRP 2012).

4 Biokinetic Modelling of Uranium in Human Body

Long-term accumulation of uranium in the human body can produce adverse health effects. The absorbed organ/tissue dose is a physical index that can be related to the risk and/or seriousness of adverse biological effects. Biokinetic models are sophisticated tools for prospective and retrospective assessment of retention of radio

elements and the calculation of tissue and organ doses following intake. They provide a mathematical platform to visualize the translocation, retention and elimination of substances within the body, considering such factors as the fractional absorption of the material via the route of entry, uptake and residence time in various tissues and organs, chemical and physical factors such as solubility and particle size distribution and clearance kinetics from the body. Thus, they assume paramount importance in predicting biological consequences of intakes and understanding the corresponding toxicity. The biokinetics of uranium is influenced by various factors such as:

- (a) Physiological characteristics of individual
- (b) Age, diet, exercise and medication
- (c) Environmental factors, such as temperature, moisture, sweating, etc.

Over the last century, much progress has been made in understanding uranium behaviour in the human body with the help of data collected from:

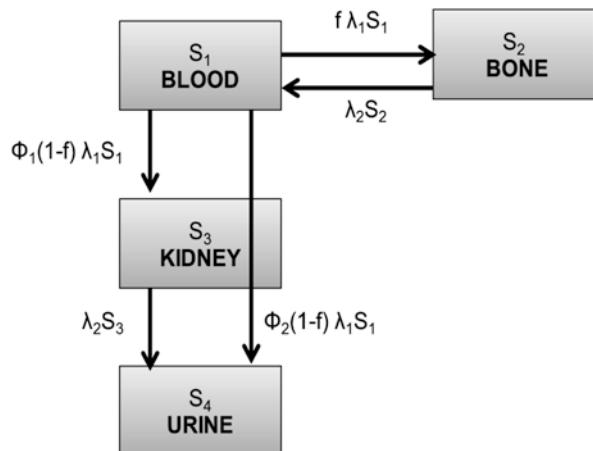
- (a) Laboratory animals such as rats, dogs and baboons exposed to uranium compounds for various experimental purposes
- (b) Measurements of uranium in blood and excreta samples of human subjects who were intravenously injected with uranium
- (c) Measurements of uranium in the respiratory tract and in urine from occupationally exposed individuals
- (d) Post-mortem measurements of tissues of occupationally exposed persons subject to inhalation or ingestion of uranium
- (e) A general understanding of physiological processes that influence uranium transport and storage in the body, e.g. through an appreciation of similarities and differences in the metabolism of calcium and uranium

The major milestones of biokinetic modelling of uranium in human adults are discussed below:

4.1 *Bernard and Struxness Model (1957)*

A cooperative study on distribution and excretion of uranium was conducted by the Department of Neurosurgery, Massachusetts General Hospital and Health Physics Division, Oak Ridge National Laboratory. Eight terminally ill brain tumour patients were administered with uranium compounds, six were injected with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and two with UCl_4 . The removal of uranium from the blood, uranium excretion in urine and faeces and distribution of uranium in the bone and in many samples of tissue were measured. A model was proposed consisting of four compartments as shown in Fig. 2 and was the first of its kind. The kidney was considered as the most susceptible organ to radiation damage rather than the bone.

Fig. 2 Schematic diagram of Bernard and Struxness (1957) model for biokinetics of uranium. Here, f is the fraction of body burden that is present in the critical organ bone; λ_i is the biological elimination constant, $i = 1, 2$; S_i is the organ burden of uranium



4.2 Lipsztein's Model (1981)

This model (Lipsztein 1981) distinguishes the human body into five different compartments: red cells, short-term bone, long-term bone, kidney and urine. The rates of transfer between these compartments are governed by first-order kinetics. The model assumes instantaneous transfer from plasma to all other compartments. Feedback from bone compartments and red cells to plasma is addressed. The gastrointestinal absorption factor, f_1 , calculated was 23%.

4.3 Wrenn's Model (1994)

Wrenn's model, as depicted in Fig. 3, forms the backbone of the ICRP's biokinetic model of uranium (ICRP 1995) although it does not address chronic environmental and occupational exposures. The key points of the model are the undivided skeleton, the aggregation of all soft tissues into a single compartment and the distinction of the kidneys into two components. The liver is not mentioned explicitly. Faecal excretion is not represented. This model substantially underestimates urinary excretion at later times, due to the slow release of a small fraction of retained uranium, mainly from the skeleton. The model is useful for interpreting results from routine urine bioassay procedures for time periods of less than 100 days post intake.

4.4 ICRP's Uranium Systemic Model

The ICRP has formulated a number of systemic models for uranium in its publications, the most noteworthy being those described in ICRP Publications 2, 30 and 69. According to the ICRP Publication 2 model (ICRP 1959), as shown in Fig. 4, 56%

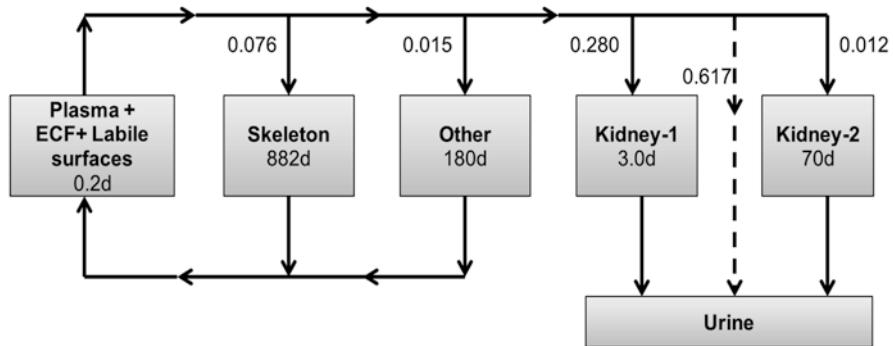
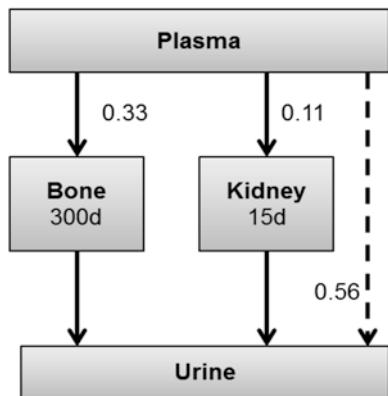


Fig. 3 Schematic diagram for the systemic biokinetics of uranium in human adults given by Wrenn et al. (1994). The periods in boxes represent biological removal half-times of respective compartments. The numbers on arrows represent the fraction of uranium transfer from one compartment to another

Fig. 4 ICRP 1959
uranium systemic model



of activity entering the systemic circulation is removed directly to excretion with a half-time of 0.25 day, 11% of the activity enters the kidney where it is retained with a half-time of 15 days and the remaining 33% reaches the skeleton where it is retained with a half-time of 300 days.

The ICRP Publication 30 biokinetic model (ICRP 1979), portrayed in Fig. 5, is the ICRP's second attempt to predict the uptake and behaviour of uranium in the human body. A uniform distribution is assumed within the bone, kidney and other soft tissue compartments. There is also urinary elimination of 0.536 of uranium entering the blood.

The ICRP's latest biokinetic model (ICRP 1995) is a sophisticated mathematical simulation that comprehensively describes the passage, fate, absorption, retention in various organs/tissues and excretion routes of uranium in a human adult following chronic intake via ingestion or inhalation. All the pathways of the uranium transpor-

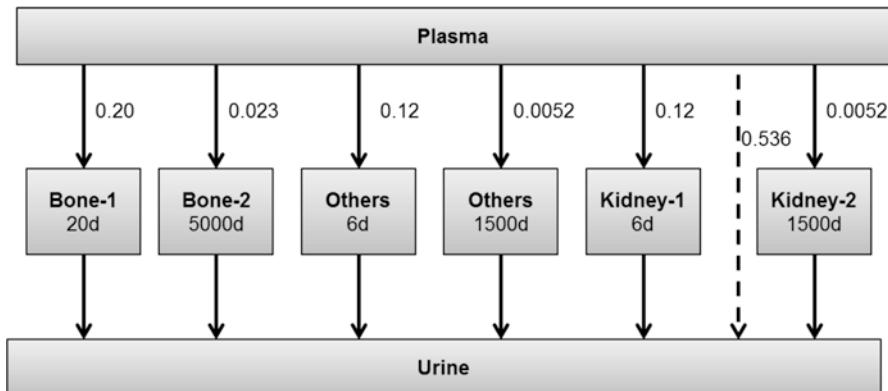


Fig. 5 ICRP 1979 uranium systemic model

tation in the ICRP's biokinetic model are based on the work of Leggett (1994) (Table 2). Plasma is regarded as a uniformly mixed pool from which uranium is removed at a rate of 35 d^{-1} . The skeleton, liver and kidneys are each modelled as two distinct compartments. The uranium deposition in the skeleton is considered to be initially on the surfaces of trabecular and cortical bone. Later, it can either return to the bloodstream or penetrate deeper into exchangeable and then nonexchangeable bone volume. The soft tissue compartments ST0 (rapid turnover), ST1 (intermediate turnover) and ST2 (tenacious retention) balance the model in terms of material distribution. Liver1 receives 1.5% of uranium leaving the circulation with removal half-time of 7 days, 93% of uranium leaving the liver is assumed to return to plasma and 7% enters Liver2, with a removal half-time of 10 years. According to this model, 63% of the uranium leaving the plasma goes directly to the urinary bladder, and 12% of that leaving plasma is eliminated from the renal tubules to the urinary bladder with a half-time of 7 days. Another kidney tissue compartment receives 0.05% of uranium leaving the circulation and is associated with a removal half-time of 5 years. The current ICRP model employs 2 and 0.2 percent as the uptake fractions from gut for soluble and highly insoluble forms of uranium, respectively, the latter being specified as uranium dioxide (UO_2) and triuranium octoxide (U_3O_8) (ICRP 1994; 1995).

4.5 Hair Compartment Model of Uranium

A hair compartment model proposed by Li et al. (2009) enhances the ICRP biokinetic model for uranium, as it includes a hair compartment for elimination in addition to faeces (GI tract) and urine (urinary bladder). It is only valid for ingestion by adults. Two input routes are assumed for the hair compartment: one directly from plasma and the other from intermediate turnover soft tissue at transfer rates $k_1 = 0.017 \text{ d}^{-1}$ and $k_3 = 13.0 \text{ d}^{-1}$, respectively. The hair growth rate is normalized at 0.1 g day^{-1} taking into account a number of factors such as type, colour, length and

Table 2 Transfer rates between various compartments used for adults in the ICRP (1995) model

Path	Transfer rate (d^{-1})
<i>From plasma to</i>	
Soft tissue, extracellular fluid (ST0)	1.05E+01
RBC	2.45E-01
Urinary bladder	1.54E+01
Kidneys (urinary path)	2.94E+00
Kidneys (other kidney tissues)	1.22E-02
Upper large intestine (ULI)	1.22E-01
Liver 1	3.67E-01
Soft tissue, intermediate turnover (ST1)	1.63E+00
Soft tissue, slow turnover (ST2)	7.35E-02
Skeleton, trabecular surfaces	2.04E+00
Skeleton, cortical surfaces	1.63E+00
<i>To plasma from</i>	
Soft tissue, extracellular fluid (ST0)	8.32E+00
RBC	3.47E-01
Kidneys (other kidney tissues)	3.80E-04
Liver 1	9.20E-02
Liver 2	1.90E-04
Soft tissue, intermediate turnover (ST1)	3.47E-02
Soft tissue, slow turnover (ST2)	1.90E-05
Bone surfaces	6.93E-02
Nonexchangeable trabecular bone volume	4.93E-04
Nonexchangeable cortical bone volume	8.21E-05
<i>Other paths</i>	
Urinary path to the urinary bladder	9.90E-02
Liver 1 to liver 2	6.93E-03
Bone surfaces to exchangeable bone volume	6.93E-02
Exchangeable bone volume to bone surfaces	1.73E-02
Exchangeable bone volume to nonexchangeable bone volume	5.78E-03

density of hair. First-order differential equations are used to represent the movement of uranium among the various compartments:

$$\frac{dq_i}{dt} = \sum_i \lambda_{ji} q_j - (\lambda_i + \lambda_r) q_i \quad , \quad i, j = 1, \dots, n \quad (5)$$

where dq_i is change in amount of uranium (in units of mass) in a particular compartment, dt is a small time interval, λ_{ji} is transfer rate between two specific compartments (from compartment j to i), λ_i is the total transfer rate from the i th compartment, λ_r is rate of radioactive decay and n is the number of compartments.

After ingestion via drinking water, the absorption of uranium occurs in the small intestine (SI) with alimentary tract transfer factor (f_1) taken as 0.6% based on epidemiological studies. From the SI, uranium enters the plasma pool and then gets distributed and reabsorbed from the soft tissues, liver, skeleton and kidneys. The hair compartment model, similarly to ICRP's biokinetic model, has a recycling nature. The set of compartments constituting the hair compartment model is illustrated in Fig. 6. This new model serves a twofold purpose:

- Excretion through urine is better represented by the biokinetic model by taking hair compartment into account.
- The uranium content in hair can provide a means for assessment of the internal body burden of uranium, both for cases of chronic exposure through ingestion and acute exposure incidents.

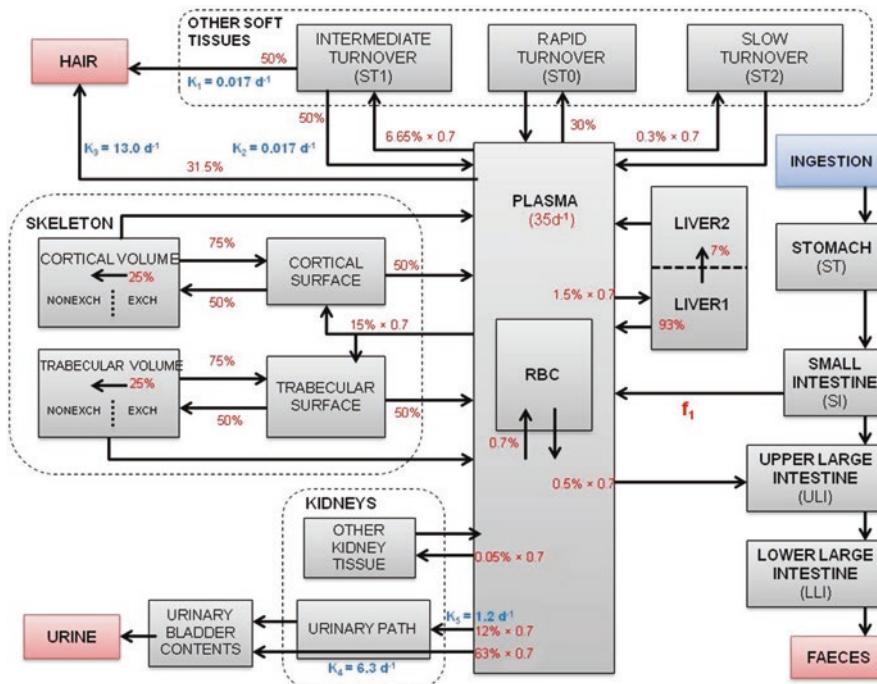


Fig. 6 Compartmental model of uranium with hair excretion pathway. The numbers in between compartments represent the fractional removal from the first compartment to the other. k_i , $i = 1, \dots, 5$ are the transfer rates exclusively used in the hair compartment model, and the rest are taken from ICRP's biokinetic model for uranium

5 Case Study

5.1 Study Area

The Malwa region of Punjab, India, has attracted widespread attention due to acute uranium poisoning of groundwater and rocketing reports of health risks. The state of Punjab lies in the north-western part of India. Stratigraphically, the Shiwalik, Piedmont and alluvial plains form three units in the state. The soil profile consists of different layers of clay, sticky clay and fine- to coarse-grained micaceous sandstone (Kochhar et al. 2006). Groundwater samples were collected from two districts of Punjab, namely, Mansa and Muktsar, in preprocessed polypropylene bottles.

5.2 Instrumentation

A LED fluorimeter was employed to determine trace levels of uranium in aqueous samples. Fluran, a buffered inorganic complexing agent of sodium pyrophosphate and orthophosphoric acid, was added to the samples to form uranium complexes. It stimulated the luminescence efficiency of uranyl ions by forming a single fluorescent uranyl species U(VI) and maintained the optimum pH for luminescence and masking efficiency. The fluorescence from organic matter was completely eliminated by using suitable optical filters and appropriate gating of the photomultiplier tube. The excitation source was a bank of pulsed LEDs emitting at 400 nm. A 6 mL water sample and 10% buffer solution were put into a cuvette for uranium analysis. Standard addition mode was followed to determine and allow for matrix effects. The details of the instrumentation and sampling procedure can be found in Kaur and Mehra (2018).

5.3 Uranium Content in Groundwater

Uranium concentrations in groundwater samples from the two districts of Mansa and Muktsar are reported in Table 3 (Bangotra 2017). The statistical parameters of the data, namely, minimum, maximum, mean and median, are 38, 436, 138.9 and 92 $\mu\text{g L}^{-1}$, respectively. The World Health Organization (WHO 2011) and US Environmental Protection Agency (USEPA 2003) have adopted maximum contaminant level (MCL) of 30 $\mu\text{g L}^{-1}$, whereas the International Commission on Radiological Protection (ICRP 1993) and United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR 2011) assigned a guideline value of 1.9 and 9 $\mu\text{g L}^{-1}$ for uranium in drinking water, respectively. However, the Atomic Regulatory Board of India, Department of Atomic Energy, India (AERB 2004), has recommended the maximum admissible concentration (MAC) for uranium in water

Table 3 Biokinetic data for ingested uranium via the drinking water pathway

Location	U conc. ^a ($\mu\text{g L}^{-1}$)	GI tract ST + SI + ULI + LLI (μg)	Blood Plasma + RBC (μg)	Skeleton Cortical bone surface (μg)	Cortical bone volume (μg)	Trabecular bone surface (μg)	Trabecular bone volume(μg)
<i>MANSA</i>							
Boha	127	1.57	0.08	0.93	165.67	1.17	44.51
Mansa	95	1.18	0.06	0.70	123.93	0.87	33.29
Fatta	245	3.03	0.16	1.80	319.60	2.25	85.86
Maluka							
Bhame	436	5.39	0.29	3.20	568.76	4.00	152.80
Dulewal	38	0.47	0.03	0.28	49.57	0.35	13.32
Jhunir	64	0.79	0.04	0.47	83.49	0.59	22.43
Bikhi	48	0.59	0.03	0.35	62.62	0.44	16.82
Sanga	70	0.87	0.05	0.51	91.32	0.64	24.53
Ralla	57	0.71	0.04	0.42	74.36	0.52	19.98
Mirpur	123	1.52	0.08	0.90	160.45	1.13	43.11
Mansa							
<i>MUKTSAR</i>							
Lambi	198	2.45	0.13	1.45	258.29	1.82	69.39
Muktsar	385	4.74	0.26	2.82	502.23	3.53	134.93
Doda	75	0.93	0.05	0.55	97.84	0.69	26.28
Bhunder	85	1.05	0.06	0.62	110.88	0.78	29.79
Malout	167	2.07	0.11	1.22	217.85	1.53	58.53
Kalippur	220	2.72	0.15	1.61	286.99	2.02	77.10
Thandewal	87	1.08	0.06	0.64	113.49	0.80	30.49
Bitiwalla	103	1.27	0.07	0.76	134.36	0.95	36.10
Sangu	66	0.82	0.04	0.06	86.10	0.61	23.13
Gidderbaha	89	1.10	0.06	0.65	116.10	0.82	31.19

(continued)

Table 3 (continued)

Location	Kidneys (μg)	Retention (μg)	Conc. (μg)	Liver Liver 1 + Liver 2 (μg)	OST		Excretion Faeces ($\mu\text{g d}^{-1}$)	Urine ($\mu\text{g d}^{-1}$)	Hair ($\mu\text{g d}^{-1}$)
					ST1 + ST0 + ST2 (μg)	Urinary bladder (μg)			
<i>MANSA</i>									
Bohra	2.19	7.06	6.76	67.02	0.03	289.94	1.35	0.37	
Mansa	1.64	5.28	5.06	50.13	0.02	216.88	1.01	0.28	
Fatta Maluka	4.22	13.62	13.04	129.30	0.06	559.33	2.61	0.72	
Bhame	7.51	24.23	23.21	230.09	0.11	995.37	4.64	1.27	
Dulewal	0.65	2.11	2.02	20.05	0.01	86.75	0.40	0.11	
Jhunir	1.10	3.56	3.41	33.78	0.02	146.11	0.68	0.19	
Bikhi	0.83	2.67	2.56	25.33	0.01	109.59	0.51	0.14	
Sanga	1.21	3.89	3.73	36.94	0.02	159.81	0.75	0.20	
Ralla	0.98	3.17	3.03	30.08	0.01	130.13	0.61	0.17	
Mirpur	2.12	6.84	6.55	64.91	0.03	280.80	1.31	0.36	
Mansa									
<i>MUKTSAR</i>									
Lambi	3.41	11.01	10.54	104.49	0.05	452.03	2.11	0.58	
Muktsar	6.63	21.40	20.50	203.18	0.09	878.94	4.10	1.13	
Doda	1.29	4.17	3.99	39.58	0.02	171.22	0.80	0.22	
Bhander	1.46	4.72	4.53	44.86	0.02	194.05	0.90	0.25	
Malout	2.88	9.28	8.89	88.13	0.04	381.25	1.78	0.49	
Kalipur	3.79	12.23	11.71	116.10	0.05	502.25	2.34	0.64	
Thandewal	1.50	4.84	4.63	45.91	0.02	198.62	0.93	0.25	
Bitiwalla	1.77	5.73	5.48	54.36	0.03	235.15	1.10	0.30	
Sangu	1.14	3.67	3.51	34.83	0.02	150.68	0.70	0.19	
Gidderbaha	1.53	4.95	4.74	46.97	0.02	203.18	0.95	0.26	

ST stomach, SJ small intestine, ULL upper large intestine, LL lower large intestine, OST other soft tissue

^aSource: Bangotra (2017)

as $60 \mu\text{g L}^{-1}$. Evidently, the uranium concentration in all, or nearly all, groundwater samples is much above the maximum acceptable values of WHO, USEPA, ICRP, UNSCEAR and AERB, India.

5.4 Biokinetic Behaviour

The biokinetic behaviour in the human body following chronic intake for 60 years via the drinking water pathway has been estimated using Li's hair compartment model, and results are summarized in Table 3.

Uranium Burden in Different Compartments in Human Body

GI Tract

The gastrointestinal tract comprising of the stomach, small intestine (SI), upper large intestine (ULI) and lower large intestine (LLI) is the first recipient of ingested uranium. The range of uranium retention in GI tract was 0.47 to $5.39 \mu\text{g}$. Significant absorption of uranium begins in the small intestine. Absorption appears to be maximum for uranium ingested in the chemical form of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, UO_2F_2 , or $\text{Na}_2\text{U}_2\text{O}_7$, roughly half as great for UO_4 or UO_3 and 1–2 orders of magnitude lower for UCl_4 , U_3O_8 , UO_2 and UF_4 (Leggett and Harrison 1995).

Blood

The least significant retention of uranium in the human body takes place in the plasma, as is proved by average value of $0.09 \mu\text{g U}$ following 60 years of chronic water intake. A secular equilibrium exists between ionic uranyl hydrogen carbonate complex and uranyl-albumin complex in the blood plasma (Moss et al. 1983). Plasma acts as a transport medium for soluble uranium complexes with citrate, bicarbonates and transferrin (protein) among the tissues and organs of deposition (Chevari and Likhner 1968; Stevens et al. 1980; Cooper et al. 1982).

Liver

The liver is classified into two compartments—Liver1 and Liver2—on the basis of their biological removal half-times of 7 days and 10 years, respectively. The range of uranium retained in both liver compartments combined is 2.02 – $23.21 \mu\text{g}$ with an average of $7.40 \mu\text{g}$, which accounts for 2.33% of the whole body retention.

Kidneys

The chief targets of uranium toxicity in the human body are the proximal convoluted tubules in the kidneys where bicarbonate uranium complexes degrade due to secretion of protons (ATSDR 1999; Aschner and Jiang 2009). The model projects average values of kidney retention and kidney concentration in members of public as 2.39 µg and 7.72 ng g⁻¹ of kidney tissues, taking the total mass of both kidneys as 310 g. As calculated by the hair model, the uranium concentration in the kidneys at all times and for all water samples is less than the nephrotoxicity standard of 0.3 µg g⁻¹. Nephrotoxic effects of uranium may include cell necrosis and tubule degeneration, leading to elevated levels of glucosuria, proteinuria, B2-microglobulin, BUN (blood urea nitrogen) and NPN (nonprotein nitrogen) (ATSDR 1999).

Skeleton

Ingested uranium is osteotropic as UO₂²⁺ mimics Ca²⁺. In the present case study, the mean value of uranium present on the cortical and trabecular bone surfaces is 1 and 1.27 µg, respectively. Moreover, the uranium contents in non-exchangeable cortical and trabecular bone volume are 181.2 and 48.68 µg. These data agree with the assumption in the ICRP biokinetic model for uranium that the removal of uranium from the non-exchangeable bone volume is very low. The non-exchangeable compartment of the skeleton is indeed the most stable storehouse of uranium in the human body.

Other Soft Tissue (OST)

OST includes the skin, muscle, subcutaneous fat and all other remaining soft tissues not explicitly assigned a compartment in the hair model. Soft tissue compartments ST0, ST1 and ST2 represent rapid (2 h), intermediate term (20 days) and tenacious retention (100 years), respectively. OST has the second highest build-up of uranium after cortical bone volume with magnitude ranging from 20.05 to 230.09 µg. 30% of uranium from plasma is delivered to ST0 in the early circulation of soluble uranium.

Urinary Bladder

Uranium may be taken up directly from plasma or indirectly from kidneys into the bladder with transfer rates $k_4 = 6.3 \text{ d}^{-1}$ and $k_5 = 1.2 \text{ d}^{-1}$, respectively, as reported in the hair compartment model. The three main processes participating in urine formation are glomerular filtration, secretion from peritubular capillaries to nephrons and, finally, the reabsorption from nephrons back to peritubular capillaries. 63% of uranium is excreted in urine via the bladder.

Time-Dependent Alteration of Uranium Load

The alteration in amount of uranium loaded in various body tissues/organs with time is encapsulated in Fig. 7. Cortical bone volume and soft tissues do not reach steady-state equilibrium even after 60 years of uninterrupted uranium exposure. In contrast, the trabecular bone volume, kidney and liver saturate. The maximum amount of natural uranium clings to the cortical bone volume at all times.

The log scale plot in Fig. 8 depicts clearly that during early stage, kidneys bear more uranium load than the liver. However, after 750 days (approx.), the situation reverses until uranium content saturates in both compartments.

Transfer Coefficients

The transfer coefficient f , also called the rate coefficient, is calculated as the ratio of uranium content in a particular organ to amount of uranium consumed daily by the person. In the present case study, transfer coefficients for the kidney, liver, skeleton, GI tract, soft tissue, urinary bladder and blood have been calculated and compared with those from previous studies in Table 4.

The value of ' f ' observed for the GI tract is the same as that obtained by Jakhu et al. (2016), but that for the urinary bladder shows a tenfold decrease. The transfer factor is highest for skeleton and least for the urinary bladder, which supports the trend of calculated uranium retention in the different tissues and organs. The wide variation in values of ' f ' for different tissues and organs points to the fact that the biokinetics of uranium varies from organ to organ.

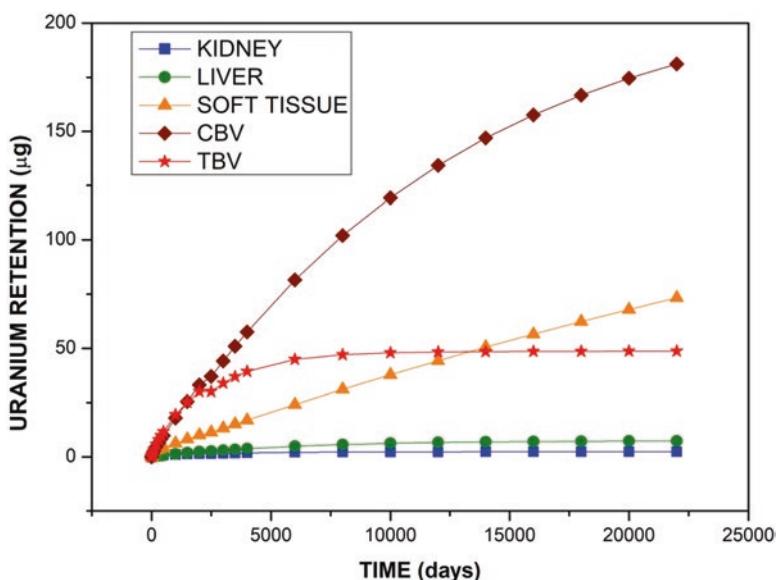


Fig. 7 Variation of uranium load in different human body compartments with time

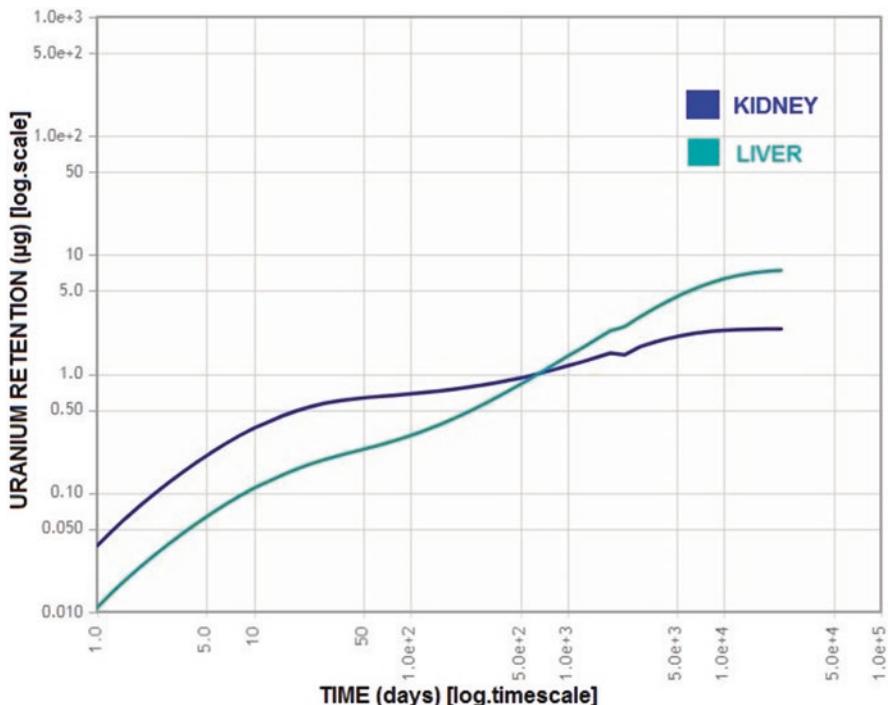


Fig. 8 Time-dependent variation of uranium load in the kidney and liver

Table 4 Comparison of transfer coefficients to various organs/tissues with previous studies

Reference study	Kidney	Liver	Skeleton	GI tract	Soft tissues	Urinary bladder	Blood
Utah ^a	0.19	0.14	3.69				
Colorado ^a	0.08	0.13	4.86				
Pennsylvania ^a	0.09	0.15	5.34				
Rajasthan (India) ^b	0.07	0.15	4.61	0.01	1.45	0.002	
Present study	0.01	0.04	1.21	0.01	0.38	0.0002	0.005

^aSingh et al. (1986)

^bJakhu et al. (2016)

Removal of Uranium from the Body by Various Excretory Paths

The excretion rates of natural uranium via three different pathways, i.e. urine, faeces and hair, are tabulated in Table 3. The excretion rate by means of hair shows a range of values from 0.20 to 2.35 $\mu\text{g d}^{-1}$ with mean and median as 0.75 and 0.50 $\mu\text{g d}^{-1}$, respectively. However, in faeces and urine, the average amount of uranium excreted from the body per day is 1.48 and 0.41 μg , respectively. Clearly, much more uranium is eliminated from the human body through the large intestine than any other route, but this is mainly unabsorbed uranium. The variation of uranium excretion

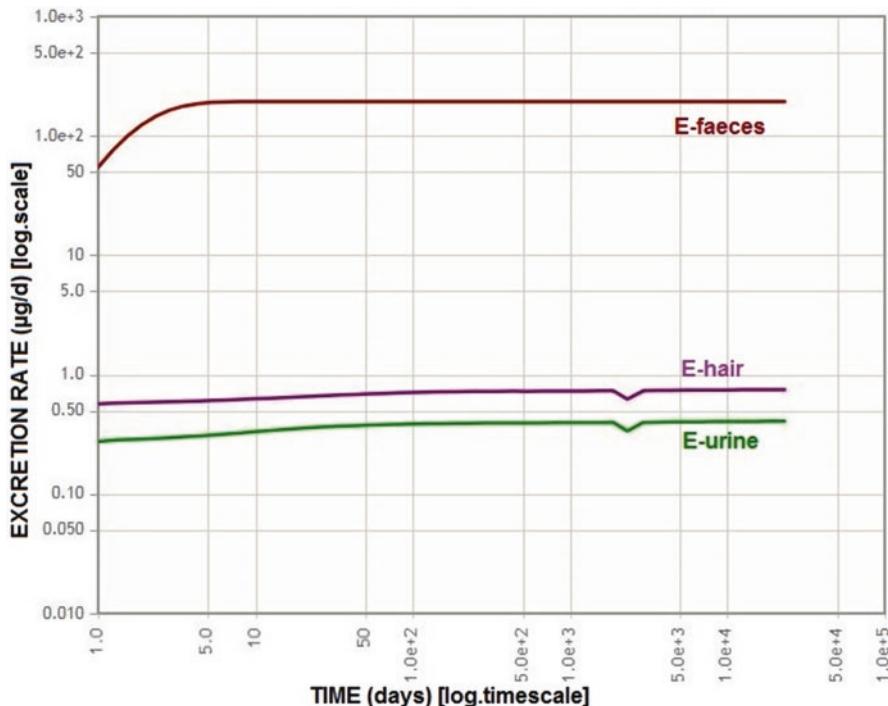


Fig. 9 Time-dependent variation of excretion rate of uranium via different routes

rates via different routes is plotted in Fig. 9. It can be safely concluded that the excretion rates are almost constant except during first few days of ingestion.

5.5 Doses to Internal Organs/Tissues

The radiological toxicity of uranium may overshadow its chemical toxicity in case of exposure to enriched uranium or exposure through inhalation of insoluble uranium compounds and their subsequent long-term retention in the body. Internal dosimetry is facilitated by using the results of biokinetic modelling. Doses to various organs/tissues of an adult human depend upon the type of intake (acute or chronic), pathway of intake (ingestion, inhalation, injection or wound), time of intake (elapsed time from exposure to measurement), physical (particle size) and chemical properties of the contaminant involved. The dose coefficients given by Li et al. (2009) were used to compute organ-specific doses in a human adult, and results are summarized in Table 5. Po-210 is the major offender for radiation dose to all organs/tissues except for skeleton where Pb-210 tyrannizes. The annual effective dose to the whole body due to uranium ingestion via drinking water pathway

Table 5 Doses to various organs and tissues of a human adult from ingested uranium via drinking water pathway

Location	Adrenals (μSv)	Bladder wall (μSv)	Bone surface (μSv)	Brain (μSv)	Breasts (μSv)	St^a Wall (μSv)	St^b wall (μSv)	ULJ^c wall (μSv)	LLJ^d wall (μSv)	Kidneys (μSv)	Liver (μSv)	Lungs (μSv)
<i>MANSAR</i>												
Boha	9.6	9.6	275.8	9.6	9.6	11.2	13.5	34.1	82.7	99.0	37.3	9.6
Mansa	7.2	7.2	206.3	7.2	7.2	8.4	10.1	25.5	61.9	74.0	27.9	7.2
Fatta	18.5	18.5	532.1	18.5	18.5	21.6	26.0	65.7	159.6	190.9	72.0	18.5
<i>Maluka</i>												
Bhame	32.9	32.9	946.9	32.9	32.9	38.4	46.2	117.0	284.1	339.8	128.1	32.9
Dulewala	2.9	2.9	82.5	2.9	2.9	3.3	4.0	10.2	24.8	29.6	11.2	2.9
Jhunir	4.8	4.8	139.0	4.8	4.8	5.6	6.8	17.2	41.7	49.9	18.8	4.8
Bikhi	3.6	3.6	104.2	3.6	3.6	4.2	5.1	12.9	31.3	37.4	14.1	3.6
Sanga	5.3	5.3	152.0	5.3	5.3	6.2	7.4	18.8	45.6	54.5	20.6	5.3
Ralla	4.3	4.3	123.8	4.3	4.3	5.0	6.0	15.3	37.1	44.4	16.7	4.3
Mirpur	9.3	9.3	267.1	9.3	9.3	10.8	13.0	33.0	80.1	95.9	36.1	9.3
<i>MUKTSAR</i>												
Lambi	14.9	14.9	430.0	14.9	14.9	17.5	21.0	53.1	129.0	154.3	58.2	14.9
Muktsar	29.0	29.0	836.1	29.0	29.0	33.9	40.8	103.3	250.8	300.0	113.1	29.0
Doda	5.7	5.7	162.9	5.7	5.7	6.6	8.0	20.1	48.9	58.4	22.0	5.7
Bhunder	6.4	6.4	184.6	6.4	6.4	7.5	9.0	22.8	55.4	66.2	25.0	6.4
Malout	12.6	12.6	362.7	12.6	12.6	14.7	17.7	44.8	108.8	130.1	49.1	12.6
Kalipur	16.6	16.6	477.8	16.6	16.6	19.4	23.3	59.0	143.3	171.4	64.6	16.6
Thandewal	6.6	6.6	188.9	6.6	6.6	7.7	9.2	23.3	56.7	67.8	25.6	6.6
Bitiwalla	7.8	7.8	223.7	7.8	7.8	9.1	10.9	27.6	67.1	80.3	30.3	7.8
Sangu	5.0	5.0	143.3	5.0	5.0	5.8	7.0	17.7	43.0	51.4	19.4	5.0
Gidderbaha	6.7	6.7	193.3	6.7	6.7	7.8	9.4	23.9	58.0	69.4	26.2	6.7

Location	Muscle (μSv)	Ovaries (μSv)	Pancreas (μSv)	Red marrow (μSv)	Skin (μSv)	Spleen (μSv)	Testes (μSv)	Thymus (μSv)	Thyroid (μSv)	Uterus (μSv)	Remainder (μSv)	Eff. dose (μSv)
<i>MANSA</i>												
Boha	9.6	9.6	9.6	29.2	9.6	9.4	9.6	9.6	9.6	10.5	21.1	
Mansa	7.2	7.2	7.2	21.8	7.2	7.2	7.0	7.2	7.2	7.9	15.8	
Fatta Maluka	18.5	18.5	18.5	56.3	18.5	18.2	18.5	18.5	18.5	20.3	40.7	
Bhame	32.9	32.9	32.9	100.3	32.9	32.9	32.3	32.9	32.9	36.2	72.4	
Duleval	2.9	2.9	2.9	8.7	2.9	2.9	2.8	2.9	2.9	3.2	6.3	
Jhunir	4.8	4.8	4.8	14.7	4.8	4.8	4.7	4.8	4.8	5.3	10.6	
Bikhi	3.6	3.6	3.6	11.0	3.6	3.6	3.6	3.6	3.6	4.0	8.0	
Sanga	5.3	5.3	5.3	16.1	5.3	5.3	5.2	5.3	5.3	5.8	11.6	
Ralla	4.3	4.3	4.3	13.1	4.3	4.3	4.2	4.3	4.3	4.7	9.5	
Mirpur Mansa	9.3	9.3	9.3	28.3	9.3	9.3	9.1	9.3	9.3	10.2	20.4	
<i>MUKTSAR</i>												
Lambi	14.9	14.9	14.9	45.5	14.9	14.9	14.7	14.9	14.9	16.4	32.9	
Muktsar	29.0	29.0	29.0	88.5	29.0	29.0	28.5	29.0	29.0	32.0	63.9	
Doda	5.7	5.7	5.7	17.2	5.7	5.7	5.6	5.7	5.7	6.2	12.5	
Bhunder	6.4	6.4	6.4	19.5	6.4	6.4	6.3	6.4	6.4	7.1	14.1	
Malout	12.6	12.6	12.6	38.4	12.6	12.6	12.4	12.6	12.6	13.9	27.7	
Kalipur	16.6	16.6	16.6	50.6	16.6	16.6	16.3	16.6	16.6	18.3	36.5	
Thandewal	6.6	6.6	6.6	20.0	6.6	6.6	6.4	6.6	6.6	7.2	14.4	
Bitiwalla	7.8	7.8	7.8	23.7	7.8	7.8	7.6	7.8	7.8	8.6	17.1	
Sangu	5.0	5.0	5.0	15.2	5.0	5.0	4.9	5.0	5.0	5.5	11.0	
Gidderbaha	6.7	6.7	6.7	20.5	6.7	6.7	6.6	6.7	6.7	7.4	14.8	

^aSt stomach^bSI small intestine^cULI upper large intestine^dLLI lower large intestine

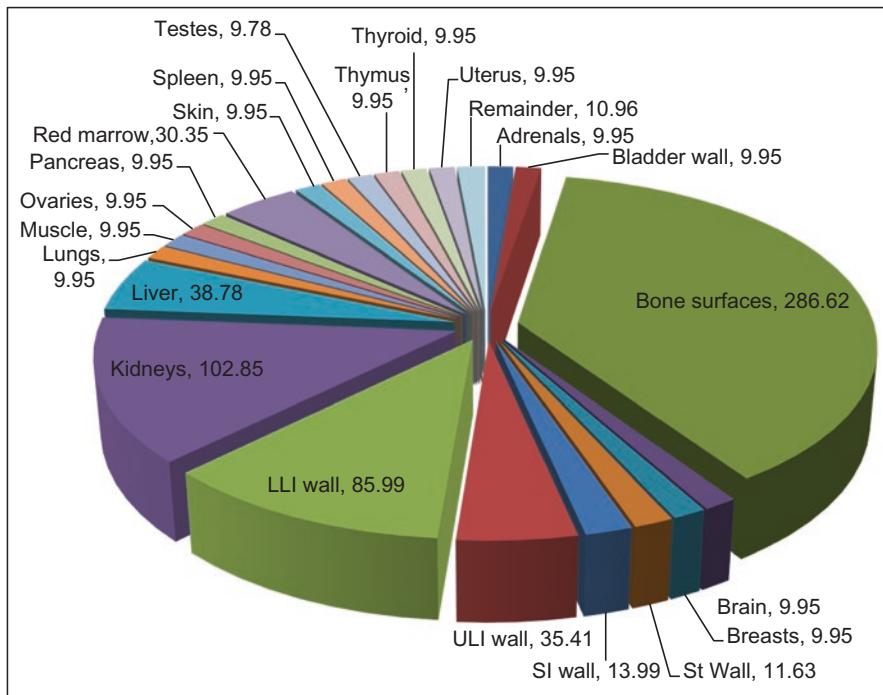


Fig. 10 Pie chart showing the distribution of total effective dose (in μSv) to different tissues and organs of the human body

ranges from 6.3 to 72.4 μSv with an average of 23.07 μSv which is safely below the recommended limit of 100 μSv (WHO 2004). The distribution of effective dose to major tissues and organs is sketched in Fig. 10. Bone surfaces are the major dose recipients (38%) due to uranium and its daughters followed by the kidneys (14%), large intestine (11%), liver (5%), stomach wall (2%) and small intestinal wall (2%). An appreciable amount of uranium in the blood (about 31.5%) is excreted through hair and does not deliver dose. Consequently, the dose coefficients calculated using the hair model have lower value than those obtained using the ICRP's biokinetic model.

6 Summary

Biokinetic models facilitate our understanding of the absorption, retention and elimination of uranium by the human body. Internal dosimetry and prediction of uranium biochemical indicators are the main advantages of these mathematical

simulations. The case study of groundwater of two districts of Punjab, Mansa and Muktsar, raises concerns over elevated uranium contents of, and resulting deleterious biological consequences to, members of public. On the basis of hair compartment model, we can conclude that:

- (a) Cortical bone volume and soft tissue form the stable uranium repository in the human body.
- (b) Bone surfaces and kidneys are the major recipients of dose due to uranium ingestion.
- (c) Excretion rates remain fairly constant over the years via faeces, urine and hair.

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