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Redistribution of uranium and thorium by soil/plant interaction in a recultivated mining area

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ABSTRACT

During the recultivation of the uranium mining area of Kővágószőlős (Hungary), the tailings were covered with clay and loess soil layers having a thickness of 30 cm and 100 cm, respectively. In the loess covering layer, acacia (*Robinia pseudoacacia*), poplars (*Populus×albus*, *Populus×canescens*), oak (*Quercus pubescens*), silver tree (*Eleagnus angustifolia*) were planted between 1996 and 2004. In order to establish the extent of the uranium and thorium transport from the sludge to the leaves by uptake and translocation processes through roots with a length higher than 1.3 m results in a remarkable redistribution of these pollutants, a gray poplar tree, growing spontaneously in the last uncovered tailing, being selected as reference tree. The U and Th concentrations in the leaves of the above-mentioned trees, in the covering layers as well as in the original sludge were determined by inductively coupled plasma sector field mass spectrometry (ICP-SF-MS). Generally, the Th concentration of the soils was about 4 times higher than that of uranium, while uranium concentration was about 10–130 times higher than that of thorium in the leaf samples and its concentration ranged from 28 to 1045 ng g^{-1}, the last value belonging to the poplar tree growing on the last uncovered tailing. In order to assume the mobility and bioavailability of uranium if the dry leaves fall down, the uranium species in the leaves of the poplar tree growing in the uncovered reservoir were determined applying ultrasound-assisted extraction with distilled water and ammonium acetate as well as high performance liquid chromatographic (HPLC)-ICP-SF-MS technique. About 20% of total uranium could be extracted in form of uranyl cations and a presumably negatively charged uranium compound. Estimations revealed that the annual increment of U in the soil surface layer due to the dead fallen leaves in case of the investigated gray poplar (*Populus×canescens*) is about 1.2%.

1. Introduction

Though the abundance of uranium and thorium in the environment is as high as that of lead, their homogeneous distribution in the earth's crust encumbers the exploitation for industrial purposes. Due to uranium mining radon-related lung cancer risk cannot be excluded [1], as radon and thoron are an intermediate decay product of the ^{238}U and ^{232}Th, respectively. Moreover, radium-226 daughter may result in an increased risk of lymphoma and bone cancer as a consequence of high specific activity and radiotoxicity. The average uranium concentration in the earth's crust is about 1.7 mg/kg [2], meanwhile that of thorium is about five times higher [3]. Uranium mining and processing involve the removal of large amount of accompanying materials and its decay products, which has the potential to increase exposure of members of the public to natural radiation through different pathways from the ore containing uranium. The main uranium extraction/mining techniques are underground and opened-pit mining and can lead to water contamination [4]. Milling operations involve the processing of the ore to extract uranium in a partially refined form, known as yellowcake. The uranium dioxide powder used in nuclear reactors is prepared either by dry process or by wet chemical route. Of the several available wet processes, the ammonium diuranate route has been the most intensively followed [5]. At the Instituto de Pesquisas Energéticas e Nucleares (Brazil), for example, yellowcake is purified to ammonium diuranate by solvent extraction. Ammonium diuranate is converted to uranium dioxide, uranium tetrafluoride and thereafter to uranium hexafluoride. Finally, this latter compound is isotopically enriched,

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after which it is converted to ammonium uranyl carbonate and then to uranium dioxide for the manufacture of reactor fuel elements [6].

In Hungary, the search for natural sources of nuclear raw materials started in 1953. One year later, a significant accumulation of uranium ore was discovered in the Mecsek Mountain, situated in the Southwestern part of Hungary, below the village of Kővágószőlős. Extensive mining was conducted in this region between 1954 and 1997. The mine was closed in 1997 and recultivation of the abandoned mining area started right after the closure.

For uranium and thorium uptake studies, knowledge of uranium and thorium species distribution is inevitable. The chemistry of uranium in aqueous systems is mainly controlled by the pH, the redox potential and complexing agents [7]. The (hydrated) uranyl ion is the dominant aqueous species in most soils below a pH of approximately 5. At higher pH, the uranyl ion hydrolyzes, forming a number of aqueous hydroxide complexes [8,9]. For example, under oxidizing conditions and carbon dioxide, UO_2^{2+} hydrolyze forming a series of negatively charged strong hydroxocarbonate complexes [10], which facilitates separation of uranyl cations on an anionic resin [6]. For example, theoretical calculations demonstrated that six different hydroxocarbonate complexes can be formed depending on the pH of the aqueous system [11] if the total ligand concentration of uranyl and carbonate ions are 20 mmol dm^{-3} and 15 mmol dm^{-3}, respectively,

In case of ryegrass grown 28 days on soils artificially contaminated with uranyl hexahidrate, it was established that uranyl carbonate complexes and $UO_2PO_4^-$ seemed the U species being preferentially taken up by the roots and transferred to the shoots [12]. However, U speciation calculations were performed for the average soil solution composition (considering soil solution U, anionic and cationic composition and pH). The distribution of the aqueous U species was calculated using a geochemical computer code. By investigating the effects of different concentrations (25, 50, 75 and 100%) of uranium tailings conditioned with garden soil on growth and biochemical parameters in sunflower, it was established that survival of sunflower plants over 100 days on higher tailing concentrations was up to 75%, which demonstrated that sunflower may be helpful in revitalization of uranium mining waste [13]. In other similar Chinese study involving nine plant species – lupine (*Lupinus albus*), Chinese mustard (*Brassica chinensis*), clover (*Trifolium pratense*), ryegrass (*Lolium perenne*), tobacco (*Nicotiana tobacum*), amongst them local vegetables like corn (*Zea mays*), chickpea (*Cicer arietinum*) and broad bean (*Vicia faba*) – it was established by gamma-spectroscopic measurements that plants took up ^{238}U and ^{226}Ra, but ^{232}Th was less bioavailable [14] from the uranium tailings sampled between 0 and 20 cm depth. Up to now, algal biomass has also been used for U removal from waste waters [15].

As it can be seen from the above-mentioned reports, over the years only few works dealt with transfer pathways of U to plants. The aim of the present work was to establish the potential risk of uranium redistribution in the environment through the tree roots and leaves. For this purpose, the concentration of uranium and thorium was determined in the sludge, clay and loess soil samples collected from the abandoned U mine. Moreover, U and Th were determined in the leaves of tree species planted in the recultivated area for three years as well as in the leaves of a poplar tree spontaneously growing on a tailing uncovered for ten years. In order to determine the bioavailability of uranium in the dried leaves, speciation study was aimed by HPLC-ICP-SF-MS hyphenated technique.

2. Experimental

2.1. Site description and soil and leaf sampling

Recently, an excellent hydrogeological characterization of this mining area has been given by Somlai et al. [16] by reporting the results of an indoor Rn determination survey conducted among the population living in the vicinity of the abandoned mine [17] as well as of the Rn concentration in the former mining tunnel as well [18]. Successful rehabilitation of the mining area (Fig. 1) is a priority issue given the vicinity of the city of Pécs, inhabited from the Roman times. The assessment of post-mining landscapes as case studies is an important part of the evaluation of current rehabilitation practices. In the abandoned mining area of the present study, the rehabilitation started with filling and covering of the tailings of the processing plant with a clay and then with a loess layer having about 30 cm and 100 cm depth, respectively. In the next step, the covered tailings were sawn with weeds and three years after this successful operation, bushes and trees were planted on the grasslands in order to prevent runoffs and erosion. This procedure was similar to that reported by Hancock et al. [18]. The main criteria in the selection of the tree species to be cultivated were fast growing, resistance against the soil salt concentration and aridity of the region. After preliminary planting investigations and after a throughout revision one year after the phytoremediation processes, massive plantation of the rehabilitated tailings was conducted between 2002 and 2004 with about 20 species. However, the most successfully employed tree species were: poplars (*Populus*×*alba*, *Populus*×*nigra*, *Populus*×*canescens*), acacia (*Robinia pseudoacacia*), oak (*Quercus pubescens*) and silver tree (*Eleagnus angustifolia*). Poplars were planted in a 250×150 cm grid, the other species in groups in a proportion of 2–10%.

Sludge and soil samples from a recultivated site were taken in the summer of 2006 with an Ejkelkamp corer. In case of the soil samples, five samples were taken from different points of the surface layer (0–10 cm) and from the 60–90 cm depth. After removing the organic debris, average samples were made from the cores. The sludge and soil samples were dried on air and passed through a 2-mm nylon sieve before analysis.

Seven group of leaf samples were taken belonging to white poplar (*Populus*×*albus*), gray poplar (*Populus*×*canescens*), acacia (*R. pseudoacacia*), silver tree (*E. angustifolia*) and oak (*Q. pubescens*) growing in the recultivation area or in an uncovered tailing. Leaves were taken on a randomized basis and transported to the laboratory where 10–20 pieces were selected from each sample and dried at 70 °C for 72 h.

2.2. Materials, reagents and standards

Throughout the experiments deionised Milli-Q water was used. SPEX U and Th stock solutions in concentration of 1 g dm^{-3} were used. For the determination of total U and Th as well as of the extracted plant material, Tl internal standard stock solution (Merck, Germany) in concentration of 1 g dm^{-3} was diluted with Milli-Q water and Suprapur® HNO_3 solution to give 5% acid concentration. Daily dilutions of the stock solutions in the working range of 0.1 to 1 ng cm^{-3} were made with Milli-Q water. All dilutions were carried out gravimetrically. For the microwave-assisted digestions, hydrogen peroxide and hydrogen fluoride were purchased from Merck.

In order to validate the U and Th results for soil and leaf samples, an IAEA-385 certified reference material and a candidate moss reference material both supplied by the International Atomic Energy Agency were used, respectively.

Ammonium acetate used for the extraction of leaves was purchased from Scharlau (Catalonia, Spain). Pyridine and formic acid used for preparation of the mobile phase for cation-exchange chromatography were purchased from Merck (Germany).

2.3. Microwave-assisted digestion of soil and leaf samples

Uranium and thorium concentrations in soil and sludge samples were determined after total dissolution using HF/HNO_3 mixture. Known amount of sample (approximately 0.1 g) was weighed into a PFA beaker and 3 cm^3 of HF and 1 cm^3 of HNO_3 were added carefully. The sample was evaporated to almost dryness. The dissolution step was repeated once again. After evaporation, traces of HF were removed by the successively addition of 2 cm^3 HNO_3 followed by evaporation to almost dryness. The residue was dissolved in 15 cm^3 5% HNO_3 and after 3-fold dilution the uranium and thorium content was measured by ICP-SF-MS.

For analysis of leaf samples a microwave-assisted digestion procedure was applied. Approximately 0.5 g of sample was weighed into