Plant Uptake of Radioactive Elements from Soils Contaminated by Uranium Mining Industry in Buhovo, Bulgaria

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Abstract

The aim of the present study was to determine the degree of accumulation in certain agricultural plants of uranium from soil collected from the bowl of Buhovo tailing pond near former uranium processing plant "Metallurg" in Bulgaria. The measured specific activities of uranium isotopes in soil were: ^{238}U - 2489 Bq/kg, ^{235}U - 117 Bq/kg and ^{234}U - 2107 Bq/kg.

Vessel vegetation trials were carried out with three varieties of barley (F-173, F-210, „Veslets"), triticale, chard, sorrel, arugula and maize on the collected soil. The highest soil to plant transfer coefficients were determined in leafy greens (^{238}U: $2,53.10^{-3}$ - $5,97.10^{-3}$; ^{235}U: $2,56.10^{-3}$ - $6,07.10^{-3}$; ^{234}U : $2,96.10^{-3}$ - $6,06.10^{-3}$), lower in cereals (^{238}U: $1,32.10^{-3}$ - $1,99.10^{-3}$; ^{235}U: $1,50.10^{-3}$ - $2,09.10^{-3}$; ^{234}U : $1.57.10^{-3}$ - $2.49.10^{-3}$) and the lowest in maize (^{238}U: $0.50.10^{-3}$; ^{235}U: $0.56.10^{-3}$; ^{234}U: $0.59.10^{-3}$).

For leafy plants, the transfer factors for arugula and chard were up to three times higher than those for sorrel. Comparing different barley varieties, up to 50% lower accumulation was found in barley F173 than in other varieties tested.

Keywords: ^{234}U, ^{235}U, ^{238}U, uranium plant uptake

Introduction

Uranium mining and processing may cause a number of environmental problems. Common consequences are air, water and soil pollution due to physical and chemical weathering of extracted rocks as a result of the classical underground method of mining, or groundwater pollution, which by infiltration contaminates water and soils as result of so the called *in-situ* leaching method. In both cases, pollution occurs during mining, but may continue long after exploitation has ceased (Ettenhuber, Roehnsch, 1993).

Uranium mining in Bulgaria is one of the oldest in the world and dates back to 1946. 47 uranium deposits were found on the territory of the country, and most of them (over 30) were in operation.

Despite the measures undertaken so far on the elimination of environmental consequences from uranium industry, a number of problems related to the implementation of technical liquidation, water management and treatment and reclamation of contaminated soils still remain unresolved (Vapirev et al., 1993).

Increased uranium content in surface soil layers may lead to accumulation of the radionuclide and its daughter products in agricultural plants and pose radiological hazard to human health.

The aim of the present study was to determine the degree of uranium accumulation in some agricultural plants grown on soils contaminated by uranium industry and, if necessary, to grow on such soils plants that absorb the lowest amounts of the element.

Materials and Methods

Buhovo tailing pond is situated at about 500 m from the uranium processing plant "Metallurg", 15 km northeast from Sofia city in Bulgaria. The area is located on the southern slopes of Stara Planina, with an average altitude of 600 m to 700 m. The main water intake is the Yaneshtitsa River, which flows into the Lesnovska River and from there into the Iskar River. Development of uranium industry caused strong anthropogenic change of the area (Banov, Hristov, 1996; Yordanova et al., 2011). Industrial buildings, roads, embankments, a tailing pond, derivation canals, waste disposal sites along the valley of the Yaneshtitsa River, etc. were built.

The main type of soils in the studied area is the leached cinnamon forest soils, Chromic Cambisols according to World Reference Base for Soil Resources (WRB). Mechanical composition of the soils is heavy sandy-clayey to slightly clayey. The silt in the surface horizon is 35-45%, and the clay - 54-60%. The content of organic matter is low, in addition, most of it is located in the humus-accumulative horizon, and in the lower horizons its percentage decreases sharply. In the humus horizon it is 1.5-2.5%, and in the clay horizon - 0.9-1.5%. Content of total nitrogen is 0.08-1.11%.The well-defined leaching process in soils has led to a relatively deep deposition of carbonates in the profile and to a slight increase in soil acidity (pH – 6-7). The sorption capacity of the leached cinnamon soils is high and differentiated by the depth of the profile depending on the mechanical composition. It varies in the range of 30-35 meq per 100g of soil. These soils are saturated with bases of which calcium is predominating.

Pot experiments were carried out with three varieties of barley (F-173, F-210 and “Veslets”), corn, triticale, spinach, chard (*Beta vulgaris subsp. Vulgaris*), sorrel (*Rumex acetosa)* and arugula (*Eruca vesicaria sativa)* on uranium contaminated soil collected from the cup of Buhovo tailing pond. The experiments were carried out in three kilograms pots in three replications. Nitrogen, phosphorus and potassium were introduced into the soil during the vegetation period.

Agrochemical characteristics of the soil were determined by procedures validated in „N. Poushkarov” Institute of Soil Science, Agrotechnologies and Plant Protection.

Plants (stems and leaves) were dried to an air dry state.

^{238}U, ^{234}U and ^{235}U were determined by validated laboratory procedure for radiochemical determination of uranium isotopes in soils, plants, water and other environmental objects (Pimpl et al. 1992; Naydenov et al., 2010). The measurements were performed for 1000 min using low background alpha spectrometer with a PIPS semiconductor detector. The calibration was performed with a certified reference material containing plutonium-239, americium-241 and curium-244 in a 1:1:1 ratio, manufactured by Amersham. The uncertainty of results was calculated at k = 2 for 95% confidence level. The measurements are validated by annual participations in interlaboratory comparisons and proficiency test schemes.

To assess the degree of uranium accumulation in plants, the corresponding transfer factors (TF) were determined - the ratio of activity concentration in 1 kg plant (dry weight) to the activity concentration in 1 kg soil (dry weight) (Sheppard, 1980).

Results and Discussion

The main chemical characteristics of the soil used in the pot experiment are presented in Table 1.

Table 1. *Agrochemical and physicochemical characteristics of the soil*

<table>
<tr><td colspan="3">pH</td><td colspan="2">∑ N-
NH_4 + NO_3</td><td>P_2O_5</td><td>K_2O</td><td rowspan="2">Soil organic matter
%</td></tr>
<tr><td colspan="2">H_2O</td><td>KCl</td><td colspan="2">mg/kg</td><td colspan="2">mg/100 g</td></tr>
<tr><td colspan="2">7.4</td><td>6.8</td><td colspan="2">6.6</td><td>9.3</td><td>6.4</td><td>0.80</td></tr>
<tr><td>$T_{8,2}$</td><td>T_{CA}</td><td>T_A</td><td>$H_{8,2}$</td><td>Al</td><td>Ca</td><td>Mg</td><td>Base Saturation</td></tr>
<tr><td colspan="8">meq/100 g</td></tr>
<tr><td>79.05</td><td>-</td><td>-</td><td>0.0</td><td>0.0</td><td>79.0</td><td>0.5</td><td>100.00</td></tr>
</table>

Specific activity of of uranium isotopes, ^{238}U, ^{234}U and ^{235}U in soil were 2489, 2107, and 117 Bq/kg, respectively. Activity concentration of uranium-238 is 62 times higher than the average of the soils in Bulgaria - 40 Bq/kg (UNSCEAR, 2000) and at about 31 times higher than the activity measured in undisturbed soils of the area 70-90 Bq/kg (Yordanova et al., 2015) indicating the anthropogenic impact. The ratio $^{234}U/^{238}U$ is 0.85, probably due to the so-called α-recoil effect and preferential leaching of ^{234}U from damaged crystal lattice of the host mineral in the soil (Pekala et al., 2010; Suresh et al., 2013).

The data for the content of uranium isotopes in different plants (air-dry weight) are presented in Table 3 at up to 10% uncertainty at k = 2 for 95% confidence level.

Table 2. *Specific activity of uranium isotopes in plants, Bq/kg*

Sample	^{234}U	^{238}U	^{235}U	$^{234}U/^{238}U$
Corn	1.26	1.33	0.06	0.95
Barley (F-173)	3.33	3.27	0.18	1.02
Barley (Veslets)	5.20	4.97	0.24	1.05
Barley (F-210)	5.24	4.96	0.25	1.06
Triticale	4.30	4.24	0.20	1.01
Sorrel	6.24	6.29	0.30	0.99
Chard	12.78	13.54	0.64	0.94
Arugula	12.51	14.86	0.71	0.84

The lowest specific activity concentration of uranium isotopes was measured in corn, in leafy vegetables - chard and arugula, the activities were 10 times higher. In sorrel and two of barley varieties (F-210 and Veslets) the specific activities were of the same order, 5-6 times higher than in the corn. The activities in barley variety F-173 were lower than the measured in other varieties of barley and triticale.

$^{234}U/^{238}U$ activity ratio in plants was around 1, indicating the identical uptake mechanism of uranium isotopes. However in arugula, where higher accumulation of two isotopes was observed, the ratio was lower than 1 and near to that determined in the soil.

Transfer factors (TF) of ^{238}U, ^{234}U and ^{235}U in plants are presented in Fig.1.

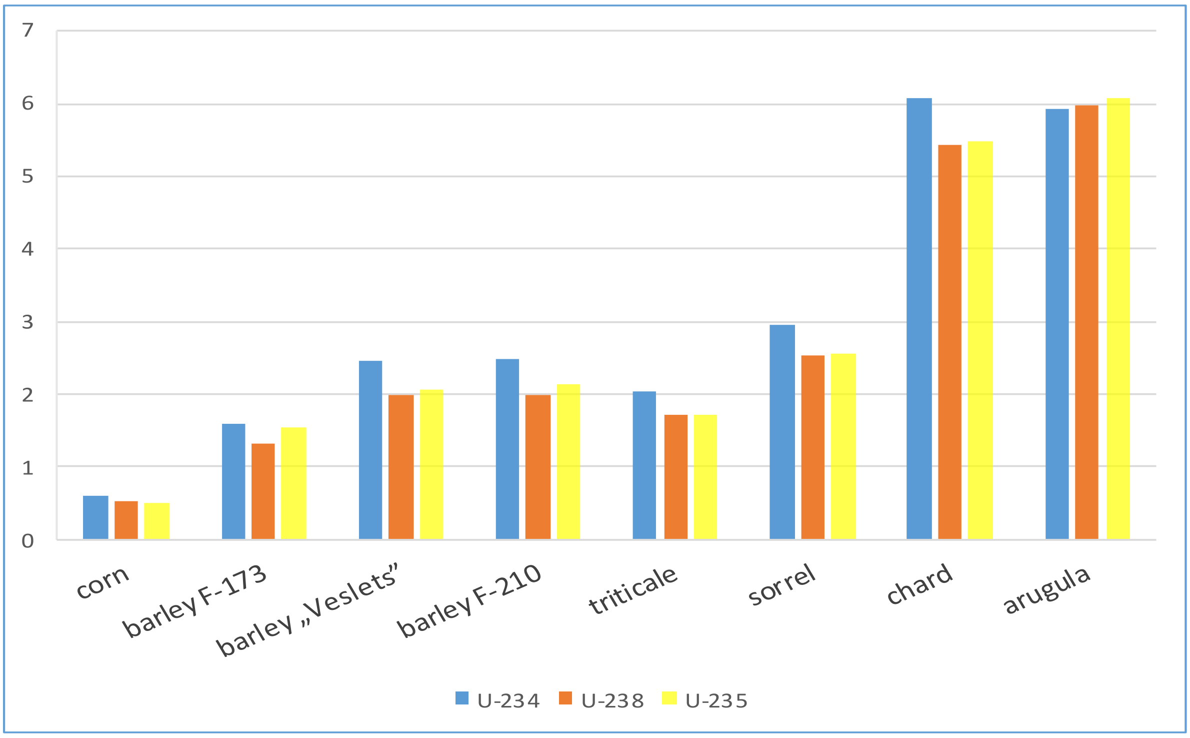

Fig. 1. *Transfer factors of uranium isotopes in plants (TF.10^{-3})*

Highest transfer factors of U isotopes were determined in leafy vegetables, a trend observed by other authors too (Anke et al., 2009; Carvalho et al., 2016).

Transfer factors of ^{234}U, ^{235}U, ^{238}U in leafy vegetables and barley were comparable - Ft = n.10^{-3}, of corn was one order lower - Ft = n.10^{-4}. Differences of around 50% were observed between barley variety - F173 and varieties F-210 and Veslets.

As it can be seen from the results obtained, TFs of uranium isotopes determined in the plants were relatively low despite the relatively high activity concentrations measured in the soil.

For example Al-Masri et al. reported ^{238}U TFs of 0.8x10^{-2} and 1.2x10^{-2} in stems of barley and wheat respectfully, grown on soils with activity concentrations of ^{238}U between 11 and 33 Bq/kg (Al-Marshi et al., 2008). The TF values of ^{234}U and ^{238}U in cereals (wheat – leaves and stems) cited by Al-Hamarnehet et al. were 0,28 и 0,29 respectfully, grown on soil with measured activities of two isotopes – 15,82 и 15,28 Bq/kg respectfully (Al-Hamarneh et al., 2016). Sasaki et al. reported TFs of 3.6x10^{-4} in spinach on soil from various districts of Japan (Sasaki et al., 2002).

In reference to soils contaminated by uranium mining industry, TFs between 0.011 and 0.023 were reported for lettuce (*Lactuca sativa L.*) grown on contaminated soils nearby abandoned mine in Cunha Baixa, Portugal (Neves et al., 2008).

In general TFs determined in the present study were lower or corresponding to the range $10^{-2} \div 10^{-3}$ cited by IAEA as parametric values for the prediction of radionuclide transfer in temperate environments (IAEA, 1994).

As it is recognized uranium transfer coefficients vary widely depending on plant species, environmental conditions, soil physical and chemical characteristics and radionuclide behavior in soil and plant.

In this context the relatively low transfer factors obtained in the present experiment could be probably explained by the following factors. Uranium is not an essential element for plant homeostasis.The availability of essential nutrients like calcium and potassium regulates the uptake of nonessential elements. The soil type under study was saturated with calcium exchangeable bases.

The availability of uranium for plant uptake from the soil solution was relatively low. Under oxidizing conditions U^{6+} is present in the form of the highly soluble uranyl ion UO_2^{2+}. It becomes even more soluble upon formation of uranyl carbonate complexes, under neutral to alkaline conditions in the soil solution. However despite the prevailing oxidizing conditions in tailings disposal sites, confinement and anaerobic bacteria activity may lead to reducing conditions resulting in precipitation of highly insoluble uraninite (Abdelouas, 2006). Coprecipitation with carbonate and phosphate (e.g. autunite, $Ca(UO_2)_2(PO_4)_2$) may also lead to uranium stabilization in mill tailings (Abdelouas et al., 1998).

Conclusion

Despite relatively high uranium activity concentrations of ^{234}U, ^{238}U and ^{235}U measured in soil, TFs of uranium isotopes determined in studied plants were relatively low and fell within the range of $n.10^{-3} \div n.10^{-4}$.

Highest uptake of uranium isotopes was found in leafy vegetables, lower in cereals, and the lowest in corn. ^{234}U,^{235}U and ^{238}U were accumulated with comparable transfer factors in leafy vegetables (sorrel, chard and arugula) - $n.10^{-3}$. In the case of corn, TF was one order lower - $n.10^{-4}$. TFs of cereals and sorrel were up to 3 times lower than these of chard and arugula.

Comparing TFs of uranium isotopes in barley varieties, up to 50% lower accumulation was found in barley F173 than in other two.

On the bases of TFs determined in the studied crops, corn, barley and triticale could be recommended for growing on the soils in the vicinity of the former uranium mine in Buhovo.

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