Thorium and uranium bioaccumulation in wheat and rye plants

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Abstract. Greenhouse pot experiments were carried out to study the mobility of U and Th in soil and the bioavailability of these radionuclides to two widely cultivated plants (wheat and rye). The purpose of this research was to estimate an ability of the crops to accumulate U and Th, thus removing these metals from contaminated soil. Rye and wheat grown in radionuclide-enriched soils demonstrated a significant increase in concentrations of U and Th in the roots of both these plants. Th was less available for plant uptake than U. The ratios of radionuclide concentrations in roots of the plants grown in contaminated soil to those in roots of the control plants were 45 (U) and 25 (Th). Despite such a significant increase of radionuclide concentrations in the plants, the U content in the soils decreased by only two times, and the Th concentration in the contaminated soils remained unchanged. No transfer of U and Th to plant leaves was detected in any of the plants. As a result of soil contamination at trace levels, wheat and rye were able to accumulate U and Th in the roots but were unable to translocate these radionuclides to leaves at measurable concentrations.

1. Introduction

Environmental pollution is a global problem resulting from mining, industrial, agricultural and military activities. Radioactive contamination is among the main sources of environmental pollution, which can seriously threaten human health. The restoration of contaminated soils is difficult and expensive. Phytoremediation is a promising in situ technology where plants are used to facilitate removal of metals from contaminated soils [1]. The plant root system induces a gradient of water flow through soil toward the plant root surface. This flow of water can remove a portion of metals from the soil. Then metals may be taken up by roots and transferred to the upper parts of the plant. The removal of radionuclides from soils is an area in which phytoremediation may have a particular impact due to the lack of alternative effective technologies.

Uranium and thorium are common natural radioelements. These radionuclides are present in soil in varying concentrations, related to the nature of the parent rocks during soil genesis. U is naturally present at low concentrations in the global environment, but is generally more abundant than metals such as Sn, Cd, Hg and Pb. Th is surprisingly abundant in the Earth's crust, being almost as abundant as Pb and three times more abundant than U. The data on distribution of U and Th in plants have been demonstrated in many scientific publications [2–6]. These long lived naturally occurring radionuclides may get transferred to plants along with the nutrients during mineral uptake, and then may be accumulated in different plant parts, thus removing these metals from contaminated soil. Although under normal environmental conditions, levels of U and Th concentrations in native plants are generally very low, there are numerous reported data on increased uptake of U and Th by plants growing in contaminated soils [7–9]. This work was undertaken to study the mobility of U and Th in soil and their bioavailability to two widely cultivated *Porceae* plants (wheat and rye). The purposes of the research were (1) to estimate an ability of the crops to accumulate U and Th, thus removing these radionuclides from contaminated soil and (2) to determine the effects of radionuclide bioaccumulation on uptake of other nutrients and trace elements by the plants.

2. Materials and methods

Greenhouse pot experiments were carried out in October 2005. Seeds of wheat (*Triticum aestivum* L.) and rye (*Secale cerealeis* L.) were obtained from the Microbiological Department of St. Petersburg Technical University. Seeds were germinated for five days on a moist filter paper. 5-day-old seedlings were transferred to large ceramic pots filled with soil. Before sowing, soil in the pots was watered with 500 mL of four different water solutions: 1: $Th(NO_3)_4$, 2: $(UO_2)(NO_3)_2$, 3: a mixture of nitrates of U and Th (concentrations of U and Th in the solutions were 50 mg L^{-1}) and 4: control. Each test was performed in triplicate. Initial soil samples were taken for analysis just after watering, before seedlings were transferred to soil. During the experiment, plants were watered every day with tap water. Plants and soil (from the root surface) were collected three times: within 3, 7 and 11 days after sowing. At the end of the experiment, soil from the bottom of all pots was also collected to estimate possible leaching of U and Th to deeper soil layers. Just after sampling, while the plants maintained turgor pressure, the plants were carefully washed until they were free from any visible soil particles. Then plant and soil samples were air-dried at room temperature to a constant weight and analyzed by instrumental neutron activation analysis. The samples were irradiated for 18 h (soils) and 24 h (plants) in a thermal neutron flux of $1 * 10^{14}$ $n \cdot cm^{-2} \cdot s^{-1}$ in the FRM-II reactor of Munich Technical University. The k0 method was used to calculate the concentrations of elements [10]. A statistical treatment of experimental data (the program Statistica for Windows 5.5) was used to estimate the mean concentrations of elements and differences between groups of samples. A cluster analysis was applied to assess the effects of the treatments on element behaviour in the plants.

3. Results and discussion

The mean concentrations of elements in roots and leaves of rye and wheat are presented in Tables 1 and 2. Although rye is botanically related to wheat (both belong to the tribe *Hordeae*), these two plants differ markedly in concentrations of many elements. Wheat has higher amounts of many elements than rye. This is typical for both the roots and leaves of the plants. The only exception is Na. Its higher concentration in wheat leaves than in rye leaves is statistically significant. In roots of rye and wheat, the concentration of Na is very similar. The concentrations of many elements (As, Co, Eu, Fe, Na, Sc, Ta, U and Zn) in roots of both these plants are higher than in leaves. This indicates that roots prevent the penetration of large amounts of different elements to the upper plant parts. Plants have evolved highly specific mechanisms to take up, translocate, and store various elements. The uptake mechanism is selective; plants preferentially acquire some elements over others. For example, the concentrations of essential plant nutrients such as K (and Rb, the chemical analogue of K) and Sr in leaves of rye and wheat are higher than in roots. This means that the plants use the mechanism of active transport of these elements from roots to leaves. It was surprising to find that the concentration of Sb in leaves of rye and wheat was higher than in roots. Sb is not an essential plant nutrient and this finding cannot be explained at the moment.

As one might expect, after adding U and Th to soil the concentration of these radionuclides in the soil increased significantly. Compared with the control solution, the U concentration was 6 times higher after treatment with U and 3 times higher after treatment with U+Th. The Th concentration was 5 times higher after treatment with Th and 3 times higher after treatment with U+Th. There was no leaching of these metals to deeper soil layers. The concentrations of Th and U in the bottom of all pots were approximately the same, regardless of the treatments.

Rye and wheat grown in the pots with radionuclide-enriched soils demonstrated significant increases in the concentration of Th and especially U in the roots of both plants. After addition of the mixture of U and Th to the soil, the concentrations of U and Th in the plant roots were also increased. However, this increase was less marked than in the experiments where U or Th were added to soil as single elements, probably because of competition between these metals during the uptake process. It is significant that the concentrations of U and Th in the leaves remained unchanged. This means that the transfer of these radionuclides from soil to leaves via root uptake was minimal.

TABLE 1. MEAN CONCENTRATIONS OF ELEMENTS IN RYE FOR VARIOUS WATERING SOLUTIONS (mg kg^{-1})

Element	Control solution		Solution with added U		Solution with added Th		Solution with added U+Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
As	0.43±0.11	<0.4	0.57±0.06	<0.4	0.45±0.23	<0.4	0.46±0.14	<0.4
Au	0.09±0.02*	0.19±0.11	0.12±0.03	0.16±0.10	0.16±0.12	0.13±0.12	0.14±0.02◆	0.19±0.07
Ba	25.3±3.0 [a]	35.1±0.5	20.5±7.4	28.8±12.2	33.9±8.0	34.9±8.9	18.8±2.0◆	38.0±8.5
Br	18.9±18.2 [a]	4.84±1.58	7.12±1.84	3.15±0.31	14.9±10.4	3.56±0.43	12.5±10.7	3.33±1.19
Ca,%	0.49±0.03 [a]	0.78±0.24	0.56±0.27	0.84±0.27	0.43±0.05	0.78±0.20	0.46±0.13	0.72±0.33
Ce	1.71±0.49	1.72±0.37	<5	1.82±0.70	2.21±1.69	2.10±0.82	3.01±1.99	1.60±0.63
Co	0.31±0.01 [a]*	0.08±0.01*	0.45±0.06◆	0.09±0.01	0.42±0.09	0.10±0.01	0.37±0.08	0.08±0.04
Cr	8.66±2.23	6.16±0.63	22.0±16.7	6.88±1.63	12.8±8.5	6.16±1.23	15.3±8.4	5.76±2.11
Cs	1.50±1.08	1.43±0.91	0.96±0.10	1.26±0.83	3.09±1.76	0.53±0.13	1.27±0.65	2.07±1.66
Eu	0.08±0.02 [a]*	0.03±0.01*	0.12±0.01◆	0.03±0.02	0.13±0.10	0.03±0.03	0.35±0.42	0.03±0.01
Fe	610±109 [a]*	317±86	855±160	319±88	779±14	304±29	628±179	287±122
Hf	1.16±0.40	0.94±0.19*	1.70±0.49	1.08±0.35	1.62±1.05	0.90±0.29	1.38±0.04	0.94±0.41
K,%	1.92±0.78 [a]	5.09±2.16	2.45±1.16	5.63±2.89	2.13±0.69	5.75±1.72	2.00±0.97	5.68±1.75
La	0.59±0.05	0.72±0.17*	<1	0.77±0.21	0.79±0.61	0.82±0.26	0.35±0.23	0.67±0.22
Lu	0.02±0.01 [a]*	0.05±0.01	0.05±0.01◆	0.05±0.02	0.04±0.03	0.04±0.02	0.04±0.01◆	0.04±0.01
Na,%	0.83±0.21 [a]	0.13±0.02*	0.82±0.03	0.13±0.01	1.04±0.36	0.12±0.01	0.94±0.32	0.13±0.03
Rb	22.3±3.6 [a]	36.4±14.0	25.6±6.63	38.4±17.8	23.7±4.6	38.3±10.4	19.6±6.4	36.9±8.9
Sb	0.73±0.05 [a]	1.83±0.97*	1.20±0.57	2.08±1.69	1.94±1.31	3.01±3.27	0.84±0.42	4.44±3.13
Sc	0.11±0.03 [a]*	0.03±0.01*	0.17±0.06	0.04±0.01	0.15±0.01	0.03±0.01	0.12±0.03	0.03±0.01
Sm	0.07±0.02*	0.08±0.02*	0.99±0.38◆	0.11±0.03	0.13±0.02◆	0.09±0.03	0.60±0.35	0.07±0.03
Sr	<25	16.6±5.7	<36	60.5±42.8	<21	80.2±55.3	<21	124±7
Ta	0.06±0.03	<0.05	0.14±0.09	<0.05	0.09±0.03	<0.05	0.08±0.03	<0.05
Th	0.21±0.02*	0.18±0.01	0.32±0.06◆	0.19±0.06	9.56±2.30◆	0.22±0.06	5.68±2.67◆	0.27±0.09
U	0.77±0.37	<0.40	34.2±13.8◆	0.35±0.05	1.26±0.10	0.42±0.08	17.5±12.3	0.45±0.23
Yb	0.12±0.05	0.18±0.03*	0.20±0.07	0.21±0.08	0.19±0.10	0.19±0.06	0.14±0.04	0.20±0.09
Zn	171±63 [a]	68.2±8.6	179±46	65.8±3.1	181±54	71.4±15.4	148±51	71.9±12.3

◆ Differences between the control and different treatments are statistically significant (P<0.05).
[a] Differences between roots and leaves of control plants are statistically significant (P<0.05).
* Differences between rye and wheat are statistically significant (P<0.05).

TABLE 2. MEAN CONCENTRATIONS OF ELEMENTS IN WHEAT FOR VARIOUS WATERING SOLUTIONS (mg kg^{-1})

Element	Control solution		Solution with added U		Solution with added Th		Solution with added U+Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
As	0.86±0.09	<0.4	0.75±0.26	<0.4	0.71±0.15	<0.4	0.45±0.07	<0.4
Au	0.31±0.03	0.21±0.16	0.19±0.10	0.17±0.09	0.20±0.07	0.28±0.11	0.29±0.13	0.20±0.15
Ba	27.3±3.2	32.7±15.1	19.7±3.9	30.7±9.8	29.6±16.9	32.3±19.6	32.2±15.8	33.5±13.3
Br	18.7±6.5 [a]	7.52±1.99	10.5±5.5	5.98±1.46	24.6±20.0	5.92±1.77	18.6±13.0	5.51±1.77
Ca,%	0.66±0.37	0.82±0.22	0.70±0.04	0.88±0.26	0.91±0.17	0.85±0.51	0.79±.022	0.88±0.40
Ce	2.30±1.17	2.42±0.67	3.01±2.63	2.42±0.78	2.03±0.66	3.23±0.42	3.84±1.67	2.24±0.39
Co	0.47±0.01 [a]	0.14±0.04	0.43±0.04	0.13±0.02	0.51±0.02	0.13±0.02	0.41±0.04	0.14±0.02
Cr	29.9±23.0 [a]	9.56±2.68	15.8±0.4	8.67±2.42	22.7±10.5	10.9±2.9	25.7±19.8	8.47±1.01
Cs	1.23±0.93	1.53±1.09	0.82±0.35	1.63±1.34	1.73±0.21	0.91±0.07	1.98±1.50	1.22±0.39
Eu	0.15±0.01 [a]	0.05±0.01	0.17±0.05	0.04±0.01	0.21±0.08	0.07±0.06	0.14±0.01	0.04±0.01
Fe	978±9 [a]	409±120	625±209	364±87	915±304	429±101	614±63 ◆	355±66
Hf	2.06±0.52	1.66±0.40	1.85±0.40	1.59±0.47	2.87±1.45	1.96±0.59	3.37±2.68	1.37±0.18
K,%	2.19±0.75 [a]	6.23±0.34	2.80±0.98	6.47±2.19	3.23±1.02	6.63±1.35	3.24±1.22	7.39±2.32
La	0.94±0.20	1.22±0.24	0.95±0.05	1.11±0.24	0.95±0.30	1.39±0.60	0.44±0.59	1.09±0.18
Lu	0.05±0.01	0.08±0.03	0.09±0.03	0.08±0.02	0.08±0.04	0.10±0.03	0.09±0.07	0.07±0.01
Na,%	0.80±0.14 [a]	0.06±0.01	0.54±0.13	0.06±0.01	0.91±0.42	0.06±0.01	0.83±0.15	0.05±0.01
Rb	28.8±3.5 [a]	40.1±3.7	30.6±11.1	40.8±18.8	37.2±12.4	40.3±10.1	33.9±14.5	45.9±13.8
Sb	0.82±0.45 [a]	4.13±0.62	0.85±0.34	4.64±3.50	1.99±1.29	2.68±2.18	1.51±0.48	1.17±0.60
Sc	0.20±0.01 [a]	0.05±0.01	0.13±0.05	0.04±0.01	0.18±0.08	0.08±0.03	0.11±0.05	0.04±0.01
Sm	0.14±0.02	0.15±0.02	0.76±0.10 ◆	0.15±0.03	0.16±0.05	0.19±0.06	0.56±0.28	0.13±0.01
Sr	<40	15.0±5.0	<32	27.6±15.2	<19	28.9±12.1	<25	24.7±10.0
Ta	0.10±0.01	<0.05	0.09±0.02	<0.05	0.13±0.06	<0.05	0.14±0.10	<0.05
Th	0.32±0.04	0.28±0.09	0.26±0.04	0.24±0.09	8.59±3.90 ◆	0.79±0.46	9.92±12.1	0.32±0.04
U	0.91±0.04 [a]	0.25±0.10	23.2±3.9 ◆	0.32±0.13	1.06±0.47	0.32±0.13	11.6±2.9 ◆	0.21±0.06
Yb	0.25±0.07	0.35±0.07	0.37±0.30	0.30±0.09	0.29±0.15	0.44±0.13	0.39±0.38	0.29±0.06
Zn	170±2 [a]	87.6±11.9	195±87	83.2±8.8	163±17	82.3±4.3	147±50	76.9±0.8

◆ Differences between control and different treatments are statistically significant ($P<0.05$).

[a] Differences between roots and leaves of control plants are statistically significant ($P<0.05$).

The ratios of the U and Th concentrations in the roots of wheat and rye to the concentrations of these elements in the soil where the plants were grown are shown in Fig.1. The ratios are higher for U than for Th for all the treatments and for both plant species. It has been reported that the mobility of uranium in soil is higher than the thorium mobility, regardless of the soil type [11, 12]. Th^{4+} is readily soluble, but at the same time it may be quickly adsorbed or precipitated as hydrolysate. It has been suggested [13] that the manner of migration in soil may be different for Th than for U, with Th migrating either as a negatively charged particle or as an anionic complex with organic matter. Since soil metal mobility correlates with the bioavailability of the metal to the plant certain differences in the bioavailability of U and Th can be expected.

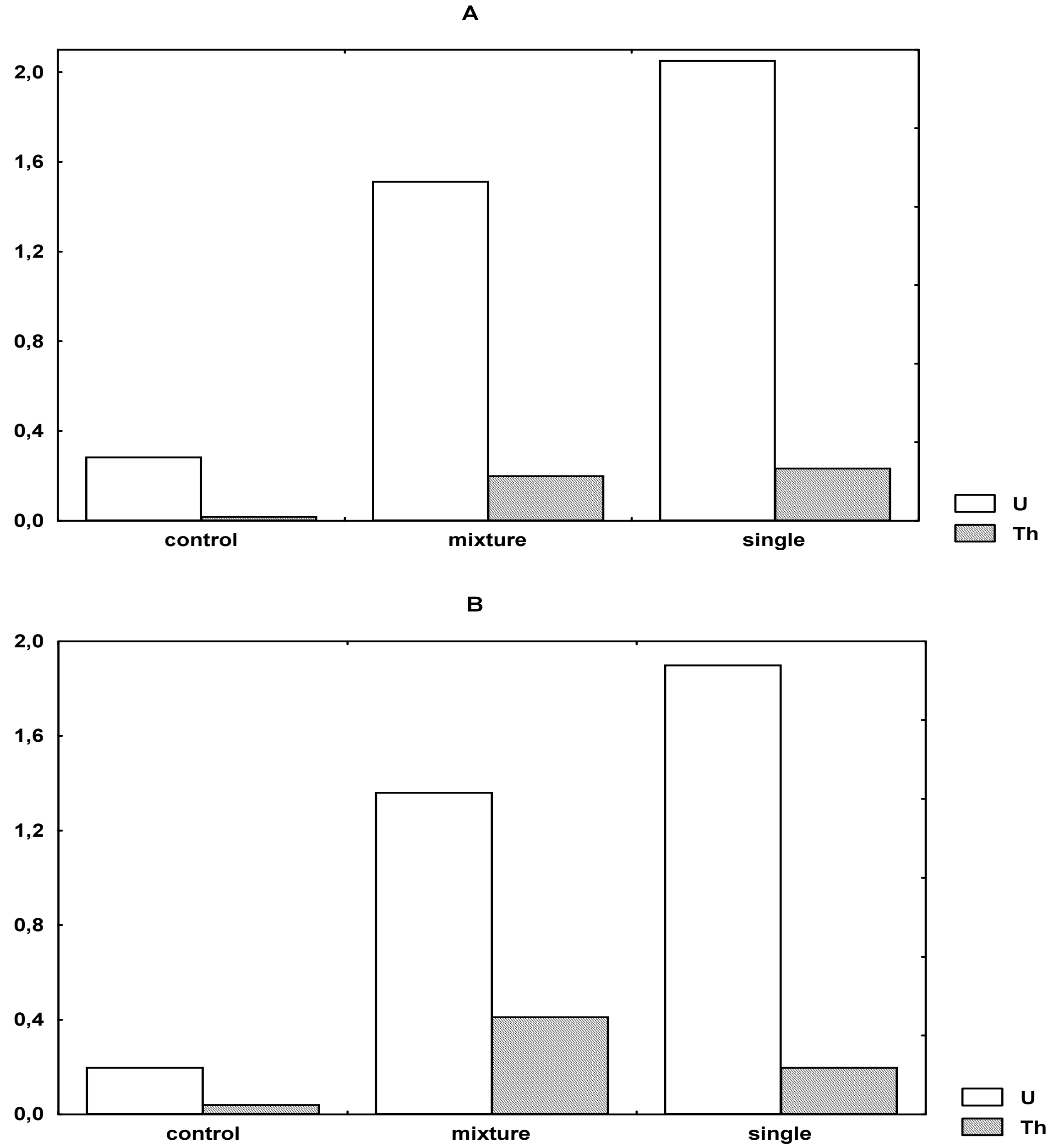

FIG.1. Ratios of U and Th concentrations in roots of rye (A) and wheat (B) grown in control and contaminated soils to the U and Th concentrations in the control soil and in the soil where U or Th (singly) or U+Th (mixture) were added.

Calculation of the soil to plant concentration ratios showed that the $U_{[root]}/U_{[soil]}$ ratios in experiments with U and U+Th are greater than unity. One might expect that such a significant uptake of U by plants could result in a decrease of U concentration in the rhizosphere soil. As an example, Fig. 2 (A) illustrates the dynamics of U in the soil where rye was grown (for the control, after adding U and after adding U+Th). With time, the soil U concentration decreased slightly in the experiment with the mixture of U and Th and decreased rather significantly in the experiment where only U was added to soil. As seen from Fig.2 (B), such a decrease in the soil U concentration resulted from uptake of U by the plant roots. The decrease was lower in the experiment with U+Th because the plants could take up less U than in the experiment with U alone.

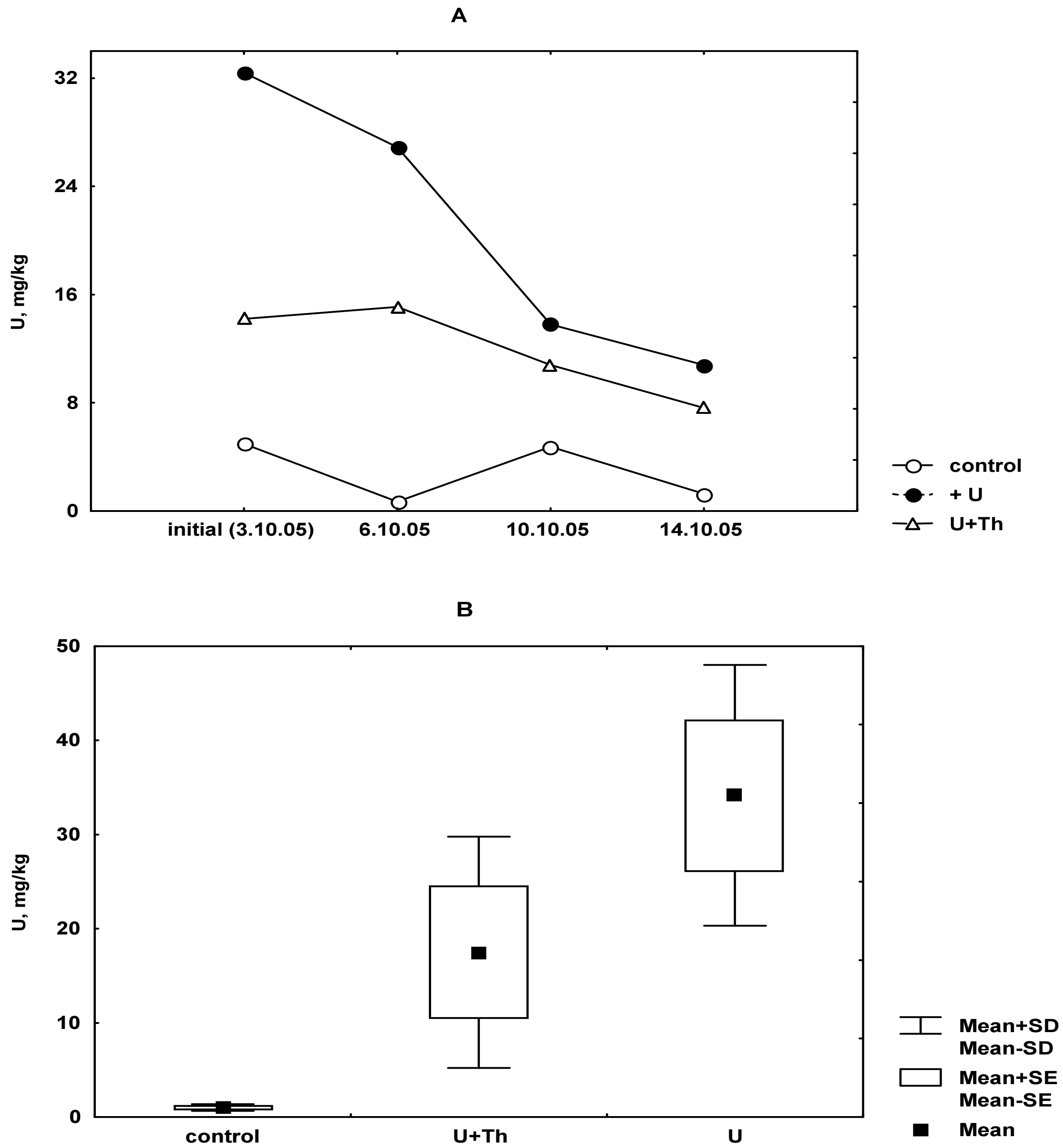

FIG.2. Dynamics of U in soil (A) and mean concentrations of U in roots of rye grown in control soil and in soil where U and U+Th were added (B).

The ratios of radionuclide concentrations in the roots of the plants grown in contaminated soil to those in the roots of the control plants are about 45 (U) and 25 (Th). This confirms that Th is less available than U for plant uptake. Despite such a significant increase of U and Th concentrations in the plants, the U content in the contaminated soils decreased only by a factor of two and Th concentration remained unchanged. Moreover, U was not transferred from roots to leaves and, therefore, it was not actually removed from the contaminated soil. The main conclusions from these observations are: (1) the biomass of the young seedlings was probably too small to clean up the large mass of the contaminated soil and (2) due to the higher mobility of U in soil and, as a result, the higher level of bioavailability of this metal to plants, U may be more easily removed from soil than Th.

Bioaccumulation of any metal in a plant can result in certain variations in concentrations of some other elements in the plant. In the experiments, roots of wheat were less affected than roots of rye. Compared with the control, there was a statistically significant increase in the concentration of Sm in the roots of the wheat grown in U-contaminated soil, while in the roots of the wheat grown in soil where U and Th were both added, the concentration of Fe was lower ($P<0.01$). In the roots of rye, more variations in element concentrations were observed after treatment of soil with U. In this case, there were statistically significant increases in the concentrations of Co, Eu, Lu, Sm, and Th over those in the control plants. The concentration of Sm in the roots of the rye grown in Th-enriched soil was higher ($P<0.05$) than the Sm content in roots of the control plants. In the roots of rye grown in the soil treated with both U and Th, the concentrations of Au and Lu increased and the Ba content decreased. The elemental composition of the leaves of the rye and wheat seedlings remained rather stable for all the treatments.

Fig. 3 illustrates the results of a cluster analysis of the leaves of rye and wheat (control plants and plants grown in U-contaminated soil). The leaves of the control plants are well distinguished into two groups: rye and wheat. We could expect such a division; it was due to differences in the concentrations of several elements in the leaves of wheat and rye (Table 1). However, there is not such a good distinction for plants grown in contaminated soil. Considering the fact that the concentrations of elements in the leaves of the plants grown in control and contaminated soils are similar, these variations are probably explained by certain changes in the relationships between elements in the plants grown in contaminated soils. Exactly the same situation is observed in the plant roots.

Acknowledgements

This work was supported by the NATO Collaborative & Linkage grant ‘Decontamination of uranium and thorium contaminated soils’.

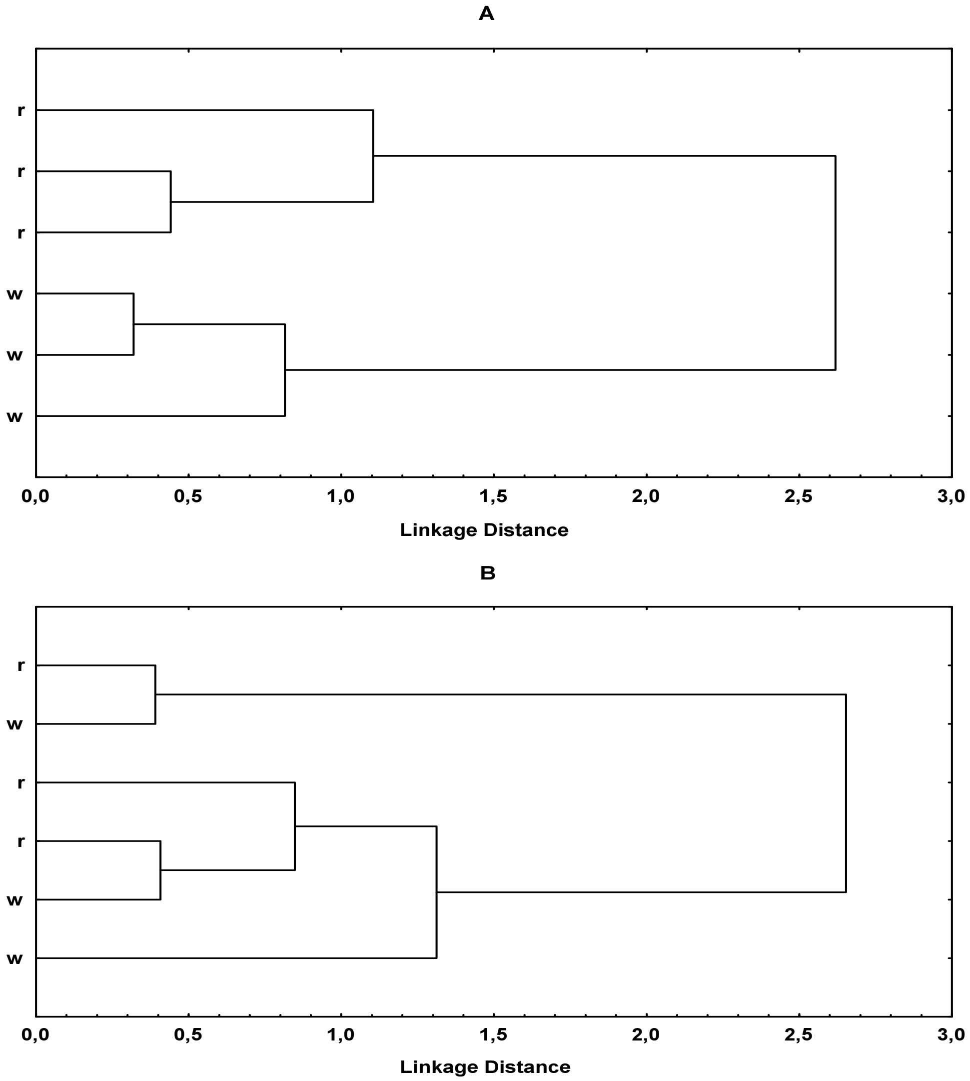

FIG.3. Cluster analysis (Ward's method) of leaves of rye (r) and wheat (w) grown in control soil (A) and in soil enriched with U (B).

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