Phytoavailability of uranium: influence of plant species and soil characteristics

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Abstract. Five plants (Maize, Indian mustard, Wheat, Pea and Ryegrass) with reported differences in uranium uptake were screened in a greenhouse experiment for their uranium soil-to-plant transfer from two soils. Soils were spiked with ^{238}U and were distinct in uranium availability characteristics. It was investigated if variability in uptake could be traced back to a different interaction of plants with the soil matrix or to different organic acid concentrations in the soils after plant growth. Clearly distinct transfer factors were obtained between soil groups which could be traced back to a difference in uranium availability between soils. However, within a soil group, there was no relation between (plant-induced changes in) soil characteristics and the transfer factors observed. The mechanisms by which the plants inhibit or promote root-shoot transfer seemed more important than soil characteristics to explain the difference in uranium transfer factor observed.

Introduction

Uranium is reported to be the most frequent radionuclide contaminant in groundwater and surface soils (Riley et al. 1992). In Europe, the major sources of soil contamination are the residues of uranium mining and milling and the residues of industries extracting or processing material containing naturally occurring radionuclides like the phosphate processing industry and the power production stations from coal.

Improper remediation of uranium contaminated areas and/or soil allocation (cattle grazing, agriculture...) may induce potential toxicological risks via the food web. Because plants represent the first step of the food web, it is essential to understand the main factors playing a role in the soil-to-plant uranium transfer. A good knowledge of parameters influencing U migration in soil and uranium uptake by plants is also important for an efficient management of contaminated areas.

Uranium uptake by plants can be expressed as a transfer factor ratio (TF: ratio Bq per g dry weight plant to Bq per g dry weight soil). The transfer factor is a global parameter; its value depends on soil characteristics like pH, carbonate content, content of phosphates, iron oxides and hydroxides, organic matter... Soil-to-plant uranium transfer is also influenced by plant physiological characteristics, such as nutrient uptake strategies and organic acid exudation. Plants have been screened for ^{238}U uptake in different plant compartments and under various experimental conditions like hydroponics (Dushenkov et al. 1995, Ramaswami et al. 2001), pot experiments (Huang et al. 1998, Ramaswami et al. 2001), and field conditions. Citric acid has been identified as the most powerful organic acid to enhance U phytoextraction (Huang et al. 1998, Ebbs et al. 1998).

In the present study, we screened the transfer factor of five plant species different in their reported uranium uptake characteristics, phylogeny and nutrient uptake strategy for two soils distinct in uranium availability characteristics. Observed transfer factors will be linked with soil characteristics and plant-induced changes of the soil environment.

Material and Methods

Two soils were used in this experiment: an acid soil with provenance the Belgian Campine Region (Plaggept) and an alkaline soil from the Belgian Loam Region (typic Hapludalf). The acid soil was characterized by a low CEC (3.77 ± 0.66 $cmol_+.kg^{-1}$), a field capacity of 123 ± 1 $ml.kg^{-1}$, an organic matter content of 2.74 ± 0.07 % and a clay content of 5.5 ± 0.1 %. For the alkaline soil a high CEC (34.98 ± 3.77 $cmol_+.kg^{-1}$), a field capacity of 182 ± 1 $ml.kg^{-1}$, an organic matter content of 4.07 ± 0.04 % and a clay content of 17.7 ± 0.4 % were observed.

About 45-kg soil batches soils were brough to field capacity, fertilized, contaminated with 330 $Bq.kg^{-1}$ ^{238}U added as uranyl nitrate hexahydrate and incubated for 3 weeks. After incubation, soils were analysed for pH and major cations (Ca^{2+}, Mg^{2+} and K^+), phosphates and total inorganic carbon (TIC) in the soil solution extracted from the soil through centrifugation. Uranium was also measured in the soil solution and in the exchangeable fraction (extraction with 1 M ammonium acetate pH 7).

A greenhouse experiment was realised with 5 plant species: Maize var. *Anjou 230*, Indian mustard var. *Vitasso*, Wheat var. *Baldus*, Pea var. *Kalife* and Ryegrass var. *Melvina*. Three pots were prepared per soil type per plant. Plants were harvested after 7 weeks, except for ryegrass which was harvested after 5 and 10 weeks. Plant shoots and roots (only for the acid soil) were weighed and dried.

Uranium content was measured in the dried shoot and root (acid soil only) samples.

Soils were analysed again at the end of the experiment after pot-dismantling for before-mentioned soil characteristics.

For the acid soil, the concentration of 4 organic acids (malate+succinate, oxalate and citrate) was measured in the soil solution following Ström et al. (2001). Malate and succinate could not be separated and are given as one common peak. Organic acid concentrations in the soil solution were expressed per gram of root.

Results

Soils

Soil characteristics before and after plant growth are listed in Table 1. A five-fold higher uranium concentration was observed for the alkaline soil (0.61 Bq L^{-1}) than for the acid soil (0.12 Bq L^{-1}). Exchangeable uranium was a factor eight higher for the alkaline soil. Comparing the soil characteristics of the acid and the alkaline soil, one would expect a higher uranium availability for the acid soil, given its low pH (4.6) and expected presence of the soluble uranyl cation (Ebbs et al., 1998) and its lower CEC, organic matter and clay content than the alkaline soil. The pH of the alkaline soil was 7.2, at which highly mobile, anionic uranyl-carbonate complexes are formed (Shahandeh and Hossner 2002). This increased solubility at higher pH must hence overrule the prevalent uranium binding properties of the soil. Total inorganic carbon and Ca content were also higher in the alkaline soil.

Uranium in the soil solution before plant growth was statistically correlated with the uranium exchangeable fraction, soil solution phosphate concentration and total inorganic carbon content.

After plant growth, uranium in the soil solution increased significantly in all treatments. Uranium enhancement was higher in acid soil (factor 18-123) than in alkaline soil (factor 9-52) for all plants. The highest soil solution uranium concentration increase was observed for wheat, with a factor 123 and 52 for the acid and alkaline soils respectively. The smallest increase was observed after growth of maize (only about ten-fold increase). Exchangeable uranium decreased slightly (~10 %) in alkaline soil but did not change in acid soil.

Soil pH tended to increase slightly (0.1-0.3 pH units) on the acid soil and decreased slightly on the alkaline soil. Soil solution phosphates content increased in the acid soil but decreased in the alkaline soil. The total inorganic carbon content (TIC) was higher in all treatments. Soil solution cation content decreased, especially in the acid soil.

Table 1. Comparison of soil characteristics following incubation, before and after plant growth. Acid = acid soil, Alk = alkaline soil. M = Maize, I = Indian mustard, W = Wheat, P = Pea and R2 = Ryegrass at second harvest. SS = soil solution, exch. = exchangeable fraction. All analyses realized in 3 replicates. SD are presented in grey below values.

Parameter	**Unit**	**Soil**	**Before**	**After**				
				M	I	W	P	R2
U SS	$Bq.L^{-1}$	Acid	0.12	2.20	5.63	14.81	8.45	4.94
			0.01	0.11	0.71	1.76	4.17	0.47
		Alk.	0.61	6.87	5.48	31.66	6.54	13.59
			0.09	1.76	0.36	3.34	3.99	1.56
U exch.	$Bq.kg^{-1}$	Acid	21	26	22	23	25	27
			1	1	1	1	1	2
		Alk.	174	155	151	150	149	140
			2	15	2	2	2	3
pH H_2O	-	Acid	4.6	4.7	4.8	4.9	4.7	4.9
			0.1	0.1	0.1	0.1	0.1	0.1
		Alk.	7.2	6.9	6.9	7.0	6.9	7.0
			0.0	0.0	0.1	0.1	0.0	0.0
HPO_4^{3-}	µM	Acid	95	153	168	164	126	169
			4	13	12	34	41	35
		Alk.	20	d.l[a]	14	d.l[a]	d.l[a]	d.l[a]
			2		1			
TIC[†]	$mg C.^{-1}$	Acid	1.1	4.0	2.0	24.7	2.8	1.9
			0.3	1.6	0.9	9.1	2.2	0.5
		Alk.	7.9	14.5	18.6	30.3	15.3	31.6
			0.5	2.6	1.9	0.8	4.4	1.4
Ca^{2+} SS	mM	Acid	15.8	0.7	0.6	0.5	0.8	0.5
			1.5	0.1	0.1	0.1	0.0	0.1
		Alk.	23.3	8.7	4.3	4.0	6.4	1.6
			0.7	0.3	0.9	0.4	1.9	0.0
Mg^{2+} SS	mM	Acid	5.4	0.2	0.2	0.2	0.3	0.1
			0.4	0.0	0.0	0.0	0.1	0.0
		Alk.	1.8	0.7	0.3	0.3	0.5	0.1
			0.0	0.0	0.1	0.0	0.1	0.0
K^+ SS	mM	Acid	12.6	0.2	0.8	1.0	1.0	0.4
			0.3	0.1	0.2	0.1	0.1	0.0
		Alk.	2.0	0.3	0.4	0.3	0.4	0.1
			0.1	0.0	0.1	0.0	0.0	0.0

[a] d.l = at least two replicates under detection limit (5.26 µM)
[†] total inorganic carbon

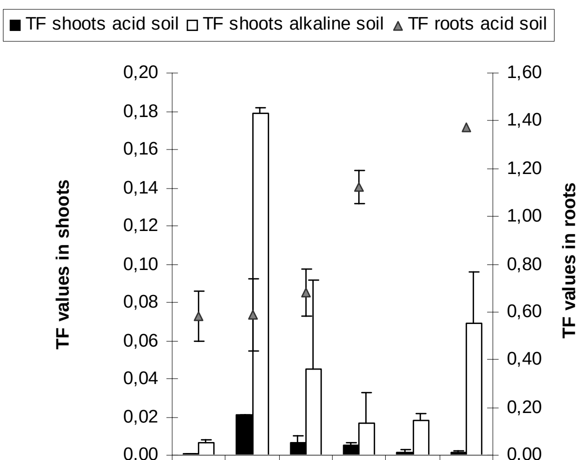
Uranium soil-to-plant transfer factors

Uranium transfer factors (TF) to roots (acid soil only) and shoots are shown in Fig.1. Three (for pea) to 35-fold (ryegrass) higher soil-to-shoot transfer factors were obtained for the alkaline soil than for the acid soil. The observed difference in shoot TFs between soils were higher than the difference in soil solution uranium concentration.

The lowest shoot-TFs on the alkaline soil were observed for maize (0.007 ± 0.003) and the highest for Indian mustard (0.179 ± 0.047). Paradoxically, the lowest soil solution uranium concentration was observed for Indian mustard. Wheat, with the highest soil solution uranium concentration after plant growth, showed the third highest uranium soil-to-shoot transfer factor. For the alkaline soil, no significant correlation was observed between the soil-to-plant transfer and any soil parameter screened.

The shoot-TFs recorded on the acid soil were also lowest for maize (0.0005 ± 0.0001) and highest for Indian mustard (0.021 ± 0.003). As for the alkaline soil, there was no agreement between the soil solution or exchangeable uranium concentration and the transfer factor observed. The soil-to-root transfer factors recorded on the acid soil only differed about two-fold between plants. The highest root TFs were observed for ryegrass (1.375 ± 0.104) and pea (1.122 ± 0.071) and the lowest for maize (0.583 ± 0.010) and Indian mustard (0.585 ± 0.151). The recorded root TFs were a factor 28 (Indian mustard) to a factor 1166 (maize) higher than the soil-to-shoot transfer factors observed.

The potential of ryegrass to transfer uranium to its shoots was very variable. No increase in uranium shoot TF was observed for the acid soil between the two harvests, whereas a nearly four-fold increase was observed at the second harvest for



	M	I	W	P	R1	R2
TF shoots acid soil	0,0005	0,021	0,007	0,005	0,0013	0,002
TF shoots alkaline soil	0,007	0,179	0,045	0,017	0,018	0,069
TF roots acid soil	0,583	0,585	0,679	1,122	*	1,375

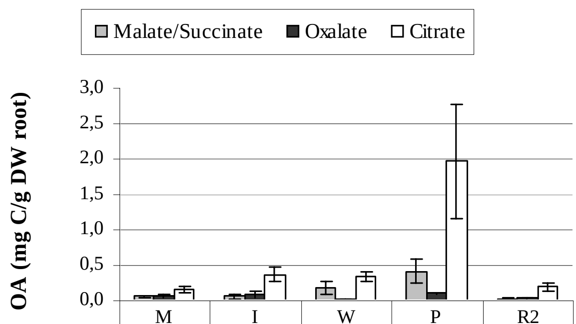
Fig. 1. U soil-to-plant transfer factors in shoots and roots (acid soil only) after greenhouse experiment on acid and alkaline soil contaminated with 330 $Bq.kg^{-1}$ ^{238}U added as uranyl nitrate. M = Maize, I = Indian mustard, W = Wheat, P = Pea, R1 = Ryegrass at first harvest, R2 = Ryegrass at second harvest. n = 3 replicates. * = no data available.

the alkaline soil, despite a 41 and 22-fold increase in soil solution uranium concentration for both soils. Possibly the bioavailability of uranium in the soil solution was more enhanced on the alkaline soil as could be inferred from the four-fold increase in total inorganic carbon content following plant growth (not observed for the acid soil) and the consequent increased presence of soluble and bioavailable uranyl carbonates uranium.

Organic acids

Fig.2. presents the concentration of organic acids in the soil solution of the acid soil at the end of the greenhouse experiment. The recorded organic acid concentrations were highly variable within treatment. The highest soil solution organic acid concentrations were observed for pea, especially for citrate. For pea we obtained important uranium concentrations in the soil solution and in the roots. Overall, however, the organic acid concentrations (total and single acid) in the soil solution were not correlated with the uranium concentration in the soil solution or the uranium uptake by roots and shoots. For example, for wheat we observed a relatively low production of citrate and other organic acids compared to pea yet a higher uranium concentration in the soil solution than pea and a medium root-TF. Ryegrass showed low organic acid concentrations in the soil solution, a low uranium concentration in the soil solution but the highest root-TF.

It should be mentioned, however, that the concentration of organic acids is highly influenced by microbial activity.



	M	I	W	P	R2
Malate/Succinate	0,06	0,06	0,18	0,41	0,03
Oxalate	0,07	0,08	0,02	0,10	0,04
Citrate	0,16	0,37	0,34	1,97	0,20

Fig. 2. Concentration of organic acids (OA) in the soil solution of acid soil after experiment expressed as mg C per g of root (dry weight). M = Maize, I = Indian mustard, W = Wheat, P = Pea, R2 = Ryegrass at second harvest. All analyses realized with HPIC. n = 6 replicates.

Discussion

The most important result concerning the evolution of soil characteristics before and after plant growth was the enhancement of the uranium concentration in the soil solution through the action of the plant roots.

In agreement with previous studies (Shahandeh and Hossner 2002), the transfer factors observed were higher for the alkaline soil than for the acid soil. This result is explained by the solubility of uranyl carbonates in alkaline soils.

Indian mustard showed the highest uranium shoot-TF on both soils and maize the lowest. However, considering all plants, the order in which they were able to transfer uranium differed between soil groups indicating that plant species react differently if the soil properties change.

Considering both soils or within each soil group, no relation was found between the (plant-induced) uranium concentrations in the soil solution and the observed transfer factors to roots and shoots. Neither the exchangeable uranium fraction, nor the organic acids recorded in the soil solution or any other soil parameter could explain the differences in transfer factors observed between plants. Prediction of the uranium phytoavailability from soil characteristics seems at this stage impossible.

The results obtained for the acid soil also point to the important influence of plant properties on the observed shoot transfer factors. The reported uranium soil solution concentration after plant growth varied about seven-fold, the root TF only about 2-fold and the shoot transfer factor fourty-fold. This means that the difference in the observed shoot concentrations or shoot TF is more influenced by plant factors than by plant-induced differences in soil characteristics. Looking at the results for Indian mustard, for example, clearly shows this. Soil solution uranium concentration was among the lowest for Indian mustard as was the observed root TF whereas the shoot TF was the highest. The ability of plants to inhibit or promote root-to-shoot transfer of uranium can be expressed by the root-shoot ratio which varied 41-fold: from 28 for Indian mustard to 1166 for maize. The mechanism by which plants can inhibit or promote root-to-shoot transfer of uranium are however not known.

Conclusions

Clearly distinct transfer factors were observed between soil groups for all plants tested which could be traced back to a difference in uranium availability and explained by soil properties, for the two distinct soils studied here.

It was, however, impossible to predict the observed transfer factors between plants from soil properties. Plants species interact differently when soil properties change. For a given soil, there was no agreement between plant-induced changes in soil characteristics and observed uptake. Not at the level of the roots but even less so at the level of the shoots since the ability of the plants to inhibit or allow root-to-shoot transfer is a more important source of variability in observed shoot TFs than is any soil characteristic.

Efforts to predict uranium transfer factors, required for the assessment of food web transfers and phytomanagement approaches, should be directed to unravel both the role of soil characteristics in affecting transfer and the mechanisms by which plants regulate internal transfer of uranium.

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