Factors affecting the plant availability of uranium in soils

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Abstract. Uranium (U) is a toxic heavy metal. The background values of natural soils differ between 0.79-11 mg kg^{-1} U. U is accumulated in the A horizons and its plant availability is influenced by both natural soil properties and anthropogenic activities. Recently, the use of phosphorus fertilizers in agriculture will be reported as a longer-term risk for the soil-plant-system. An alien source of environmental pollution results from military operations. Soil fertility, pH value and nutrient supply can effect the U content of crops growing on U contaminated soils.

Introduction

Uranium (U) is a natural constituent of the rocks in the earth's crust. Typical natural soil background values differ between 0.79-11 µg g^{-1} U, in relation to the parent material (Kabata-Pendias and Pendias 2001). U is generally accumulated in the A horizons and its plant availability is influenced by both natural soil properties and anthropogenic activities. Soil contaminations with U are a severe problem in mining areas and in the surrounding of processing plants.

Recently, new threats for the soil-plant-system have been reported. Phosphorus fertilizers commonly used in agriculture originate from rock phosphates. Besides the essential nutrient P this mineral fertilizers contain various amounts of U. Thus, it might be possible that critical contamination levels in soils result from common fertilization practices.

An alien source of environmental pollution results from military operations, in which ammunition with penetrators manufactured from depleted uranium (DU) is used. During military conflicts, e.g. in Kosovo, over 30,000 rounds of such DU containing projectiles were fired from aircraft. DU is a by-product remaining after the U enrichment process. Though its content of ^{235}U is depleted to about 0.2-

0.3 %, DU keeps an unstable, radioactive heavy metal with toxic properties influencing life processes. The majority of these above-named penetrators missed the targets (around 90%). They are still in the soil with nearly no chance of detection within the ordinary scope of search. Plant available U will be released by permanent conversion processes of DU in the active soil horizon. Concentrations of up to 400 µg g^{-1} U in the soil close to the metal projectiles were reported (UNEP 2001).

Hazardous effects on health originate if humans and animals will be contaminated by U compounds through inhalation, ingestion or skin contacts. Whereas skin contact is particularly a threat for those working in the U industry, inhalation and ingestion are probable contamination pathways for broader levels of population living in U polluted regions. Ingestion of U occurs by drinking water, and through the food chain via crop plants, animal feed, and animal products.

Uranyl (UO_2^{2+}) is the soluble form transported within the body by the blood stream and it forms complexes with protein and anions. U tends to accumulate in the body, preferentially in the liver and the kidneys. U is damaging the organism either by radioactivity, or by its biochemical toxicity as a heavy metal. The dangers arising from the biochemical toxicity of uranium are generally considered to predominate the risks from its radioactivity. The U ingestion cannot be completely avoided. It varies according to the humans' local diets: daily, up to 4 µg U will be incorporated with the solid food. In addition, the U intake via drinking water, especially mineral waters, is to consider. Even at low concentration levels drinking water accounts to more than 80% of the total U ingestion (Schnug et al. 2005; Milvy and Cothern 1990; Cothern and Lappenbusch 1983).

Heavy metals mobility is affected by the soil redox potential and thus subjected to nearly all changes in soil conditions. The conversion of the metal ionic valences leads to changes of the binding conditions within the soil minerals, resulting in more unstable and soluble forms of metal ions. Under reducing situations, many heavy metal ions form insoluble sulfide compounds, abating the risk of absorption by roots. Alterations of the soil reaction involve a changing solubility of metal cations (McLaughlin 2002). Plant available UO_2^{2+} ions will be released from the surface of soil colloids by ion exchange. After lime fertilization the UO_2^{2+} ions will be replaced by Ca^{2+} ions. In consequence of soil acidity the UO_2^{2+} ions will be substituted by H^+ ions. Microorganisms and plant roots themselves release organic compounds, e.g. phenolic acids and amino acids, which acidify the surrounding soil. Afterwards, the free metal ions will be bound within natural chelate complexes, which have a high affinity to heavy metal ions.

In such a way bounded U ions can diffuse directly through the epidermis of plant roots as well as will easily dissolve from these organic complexes by plant originated enzymes and taken up by the roots as cations.

The distribution within the stems, leaves, flowers, and storage organs occurs via the xylem. The U will be incorporated in cell membranes and vacuoles, predominantly.

Material and methods

The influence of soil fertility and fertilization on the plant availability of U in contaminated soil substrates was investigated. The effect of phosphorus (P) fertilization, liming, nitrogen (N), and sulfur (S) nutrition on growth and U uptake of different crops was tested in two multi-factorial, fully randomized pot experiments

Table 1. Set of the treatments for pot experiment 1, (detailed description see Lamas, 2005).

Experiment 1:	*Lolium perenne*; duration 2 years			
Soil fertility: High	Grassland topsoil (GT) [a,c]	U contamination [mg kg^{-1} U]: 0	P fertilization [mg kg^{-1} P]: 0	Liming [mg kg^{-1} $CaCO_3$]: 0
	Grassland subsoil (GS) [b,c]	250		
	Forest topsoil (FT) [a,d]	500	1,500	5,000
Low	Forest subsoil (FS) [b,d]	1,000		

[a] topsoil: soil depth 0…25 cm; [c] Dystric Cambisol/ Orthic Luvisol
[b] subsoil: soil depth 25…30 cm; [d] Leptic Podzol

Table 2. Set of the treatments for pot experiment 2, (detailed description see Rivas, 2005).

Experiment 2:	*Zea mays L., Helianthus annuus L., Vicia faba L.*; duration 6 weeks				
P_t in the soil [mg kg^{-1} P]: 334	U contamination [mg kg^{-1} U]:	at low P_t level	at high P_t level	N fertilization [mg kg^{-1}]: 250	S fertilization [mg kg^{-1}]: 0
	non-contaminated	non-contaminated			
1,558	166	173		500	50
	329	385			
	660	644			

(Table 1, Table 2). The differences in soil fertility arose from the sites where the substrates derived from: a natural grassland site and a forest site. At both sites, soil from different depths (0-25 cm and 25-50 cm) was removed, representing topsoil and subsoil quality.

The soil substrate used in the 2nd experiment originated from the 1st pot experiment and mixed again considering the different U contamination levels and the P fertilization treatments.

The soil substrates were contaminated before the beginning of the first experiment with the green modification of U_3O_8. This substance was gained from uranylnitrate according to the procedure reported by Fleckenstein (1972). The contamination occurs separately for each pot by mixing the corresponding portion of the oxide powder with the substrate. The plants grew in a vegetation hall under controlled water conditions. The grass yielded 6 cuts. Maize, sunflowers, and faba beans were harvested during the elongation stage (BBCH stage 32; BBCH Scale: adapted from Meier 2001). After the determination of the total dry matter yield the plant material was digested by microwave.

Before the pot experiment started the original soil substrates were analyzed for pH (soil suspension by $CaCl_2$); total C (C_t: by LECO carbon analyzer); total N (N_t: by Kjeldahl); P_{CAL}, K_{CAL} (extractable by calcium acetic lactat according to Schüller 1969).

The soil samples were digested with

- Aqua Regia (nitrohydrochloric acid) to extract the total U and P contents (U_t, P_t), and with
- AAAcEDTA (acid-ammonium-acetate-EDTA) (Lamas et al. 2002) to extract the plant available fraction ($U_{available}$, $P_{available}$).

The amount of U and P containing in the extracts of the soil and plant samples, were measured by Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS). The lowest limit of detection was estimated to 5 ng L^{-1} (Sparovek et al. 2001).

Results and Discussion

Effect of soil fertility, P fertilization and liming on the plant available U in soils

The investigated soil substrates varied in the quality-determinant properties depending on their derivation (Table 3).

Both topsoil substrates featured higher total carbon and nitrogen content. The grassland topsoil contained considerably more P_{CAL} than the other substrates. Both grassland topsoil and subsoil were higher supplied with K_{CAL} than the forest substrates. The differences between the background values of plant available U were only small.

Table 3. Characterization of the original soil substrates.

Origin	Soil type	German classification	Soil depth		pH	C_t	N_t	P_{CAL}	K_{CAL}	$U_{available}$
			[cm]			[%]	[mg g^{-1}]	[mg kg^{-1}]		
Grassland	Silty-loamy sand	Podzolic Brownearth	GT	0-25	5.9	1.2	1.0	108	261	0.02
			GS	25-30	4.8	0.5	0.4	20	246	0.03
Forest	Sandy	Podzol	FT	0-25	3.5	2.0	1.1	48	25	0.04
			FS	25-50	3.8	0.6	0.4	20	5	0.04

The artificial U contamination resulted in significantly increased $U_{available}$ contents of the untreated substrates corresponding to the U contamination levels. In GT, the substrate with the highest fertility, the lowest amounts of plant available U were determined (Table 4).

Notably higher $U_{available}$ contents were detected in the lower fertile substrates (GS, FT, FS). The deficient P contents as well as the lower pH values compared to those of GT could be the reason for the differences (Table 3).

The P fertilization in form of $CaHPO_4$ at the beginning of the experiment resulted in considerably decreased $U_{available}$ contents in the soil substrates (Table 5). Whereas in the GT substrate the U contents of all contaminated treatments decreased approx. to the half, the decreasing effect in the lower fertile substrates was extreme: up to 89 % lower contents of plant available U were measured.

The addition of $CaCO_3$ simulating lime fertilization caused only in the GT a 20 % decrease of the $U_{available}$ content (Table 5). There was a minor effect in GS and FT at the 250 mg kg^{-1} U contamination level only. In the most cases the lime addition even resulted increased values of plant available U. This is attributed

Table 4. Content of plant available U [mg kg^{-1} U] in different fertile, unfertilized soil substrates contaminated with U_3O_8; experiment 1; *Lolium perenne*, 58 weeks after the contamination, cut 7.

Soil substrate **unfertilized**	U contamination rate [mg kg^{-1} U]			
	0 (control)	250	500	1,000
		$U_{available}$ [mg kg^{-1}]		
GT	0.02	25	54	117
GS	0.03	79	130	309
FT	0.04	78	160	297
FS	0.04	86	148	317
Mean	0.03	67	123	260
$LSD_{0.05}$:		32.2		

to the raised amount of Ca^{2+} ions in these treatments. Metal ions bounded at the soil colloids were replaced by Ca^{2+} ions and released (Schroeder 1992). The portion of free UO^{2+} ions in the soil substrates was raised.

Table 5. Effect of P fertilization and liming on the content of plant available U [mg kg^{-1} U] in different fertile soil substrates contaminated with U_3O_8; experiment 1; *Lolium perenne*, 58 weeks after the contamination, cut 7.

Soil substrate **fertilized**	U contamination rate [mg kg^{-1} U]							
	control	250	500	1,000	control	250	500	1,000
	P fertilization				Liming			
	$U_{available}$ [mg kg^{-1}]							
GT	0.01	12	27	55	0.01	21	42	92
GS	0.01	15	27	77	0.03	69	145	260
FT	0.02	29	18	78	0.02	70	159	307
FS	0.03	13	33	61	0.03	87	172	313
Mean	0.02	18	26	68	0.03	62	130	243
$LSD_{0.05}$:		9.7				13.0		

Effect of soil fertility, P fertilization, and liming on the U content in plants

The U content of *Lolium perenne* increased corresponding to the increased U content of the soil substrates. This effect was even more pronounced for the plants growing in the lower fertile soil substrates (Fig.1). The highest U content was determined in grass growing at the 1,000 mg kg^{-1} U contamination level, averaged over all other treatments.

In Table 6 the U contents of *Lolium perenne* shows the main effects of the investigated treatments, calculated as mean values of all U contamination levels. The higher the natural soil fertility the lower was the detectible U content of the grass leaves. The effect of a sufficient P nutrition appeared in a significantly lower U concentration in the plants.

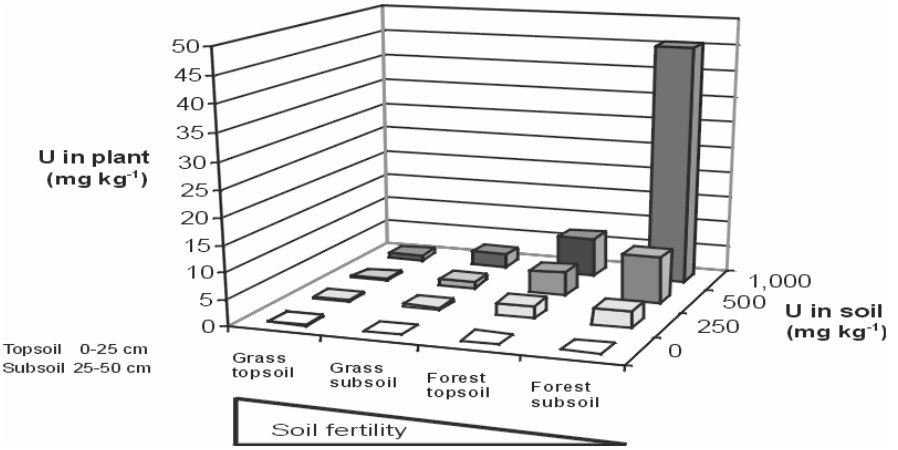

Fig. 1. Uranium concentrations in *Lolium perenne* (4th cut, 40 weeks after contamination) grown on top and subsoil material derived from grassland and forest sites with different U contamination, experiment 1.

Table 6. Effect of soil fertility, P fertilization, liming, and changing pH values on the U content in *Lolium perenne* [mg kg^{-1}], experiment 1, 50 weeks after contamination, cut 6.

U content in *Lolium perenne*, treatment averages [mg kg^{-1} U]						Soil pH
Soil substrate		P fertilization		Liming		
GT	0.27	-[a]	0.35	-	0.44	6.3
				+	0.25	6.9
		+[b]	0.18	-	0.20	6.5
				+	0.16	6.8
GS	0.90	-	1.63	-	1.72	5.0
				+	1.55	6.7
		+	0.18	-	0.14	5.6
				+	0.21	6.6
FT	1.19	-	2.22	-	3.72	3.6
				+	0.71	5.6
		+	0.16	-	0.17	4.4
				+	0.15	6.1
FS	1.64	-	3.17	-	4.89	4.2
				+	1.45	5.6
		+	0.11	-	0.11	4.9
				+	0.11	6.3

[a] -...no fertilization [b] with fertilization

The addition of lime had a comparable impact on the $U_{available}$ content in the soil. In combination with P fertilizing the decreasing effects were still enhanced. The plants growing in the corresponding treatments continuously developed more biomass due to the sufficient nutrient supply, the higher pH values of the soil substrates, and the subsequent better growing conditions. Hence, the alleviated U contents in the plant tissue are to interpret as a dilution effect. The U content of aboveground plant tissues was reduced to values given as tolerable (< 0.4 mg kg^{-1}; following Dreesen and Marple 1979).

The investigations of juvenile crops in the 2nd pot experiment documented that differences exist between several plant species in terms of their capability to absorb U from the soil (Table 7). Although, at the end of the experiment the $U_{available}$ content of the pot's soil substrates differed non significantly, the dicotyledonous species, sunflower and faba bean, showed a higher uptake ratio than the monocotyledonous maize. The amount of detectable U in the aboveground plant parts increased depending on the U contamination level, except for the legume faba bean.

In the plant species a highly raised U content was measured at the strongest U contamination level, the both lower contaminated substrates resulted in nearly unspecific differing U concentrations.

Sufficient N nutrition tested for maize and sunflowers increased the U content of in the plants. S fertilization decreased the U content of all crops, whereas the effect was clearly marked for maize.

Table 7. Effect of P, N and S nutrition on the U content in *Zea mays*, *Helianthus annuus*, and *Vicia faba* growing on soil substrates contaminated with various rates of U_3O_8, experiment 2.

Treatment levels		$U_{available}$ in soil substrate [mg kg^{-1} U]			U content in plant [mg kg^{-1} U]		
[mg kg^{-1}]		Maize	Sunflower	Faba bean	Maize	Sunflower	Faba bean
U rate effect	166/173	39.1	37.6	33.5	1.21	0.95	1.82
	329/385	78.1	76.6	74.6	1.66	2.31	1.60
	660/664	180	176	178	3.72	4.34	5.28
P effect	334	156	154	154	2.27	3.02	2.92
	1,558	41.6	39.2	37	2.00	2.04	2.89
N effect	250	101	98.1	95.3	1.71	2.01	2.90
	500	97.3	95.6		2.59	3.05	
S effect	0	99.6	98.2	92.8	3.10	3.02	3.31
	50	98.5	95.4	97.9	1.25	2.04	2.50
Crop specific effect		99.1	96.8	95.3	2.13	2.53	2.90

The investigation revealed that U incorporated in soils could be easily mobilized and absorbed by plant roots. High Ca concentrations in the soil solution can lead to a raising release of mobile uranyl ions, which are plant available. A factor limiting the soil/plant transfer is a high concentration of phosphates in the soil.

A fertilization management combining P addition with liming improves the conditions of poor soils for growing plants. The soil content of plant available U will simultaneously reduced by binding in stable phosphate complexes. A sufficient S nutrition of the growing plants seems to be another measure to minimize the U uptake by plants, and thus to avoid that the toxic heavy metal U enters the food chain via soil/plant transfer.

References

Cothern CR, Lappenbusch WL (1983) Occurrence of Uranium in Drinking Water in the U.S. Health Physics 45: 89-99

Dreesen DR, Marple ML (1979) Uptake of trace elements and radionuclides from uranium mill tailings by four-wing saltbrush (Altriplex canescens) and alkali sacaton (Sporobolus airoides). Symposium on uranium mill tailings management. Colorado State University, Fort Collins, Colorado: 127-143

Fleckenstein J (1972) Untersuchungen an Alkalioxofluorouronaten. Dissertation. Universität Tübingen

Kabata-Pendias A, Pendias H (2001) Trace Elements in Soils and Plants. CRC Press: Boca Raton, London, New York: 413 p

Lamas M (2005) Factors affecting the availability of uranium in soils. Landbauforschung Völkenrode Special Issue 278: 102 p

Lamas M, Fleckenstein J, Schroetter S, Sparovek RM, Schnug E (2002) Determination of Uranium by Means of ICP-QMS. Comm Soil Sci Plant Anal 15-18(33): 3469-3479

McLaughlin MJ (2002) Heavy Metals. In Lal, R. (ed) Encyclopedia of Soil Science. Marcel Dekker, New York, Basel: 650-653

Meier U. (2001) Entwicklungsstadien mono- und dykotyler Pflanzen, BBCH Monografie, 2. Auflage, Biologische Bundesanstalt für Land- und Forstwirtschaft.

Milvy P, Cothern CR (1990) Scientific Background for the Development of Regulations for Radionuclides in Drinking Water. In Cothern CR, Rebers P (eds) Radon, Radium and Uranium in Drinking Water. Lewis Publishers, Chelsea, Michigan: 1-16

Rivas M (2005) Interaction between Uranium Contamination and Fertilization on Uranium Content and Uptake of plants and Soil Microbial Parameters. Landbauforschung Völkenrode Special Issue: in preparation

Schnug E, Sparovek, RBM, Lamas M, Kratz S, Fleckenstein J, Schroetter S (2005) Uranium Contamination. In Lal, R. (ed) Encyclopedia of Soil Science. Marcel Dekker, New York, Basel: (in print)

Schroeder D (1992) Bodenkunde in Stichworten. Verlag Ferdinand Hirth, Berlin, Stuttgart 5th rev. ed.: 175 p

Schüller H (1969) Die CAL-Methode zur Bestimmung des pflanzenverfügbaren Phosphates in Böden. Z. Pflanzener. Bodenk. 123(1): 48-63

Sparovek RBM, Fleckenstein J, Schnug E (2001) Issues of Uranium and Radioactivity in natural waters. Landbauforschung Völkenrode 4(51): 149-157

UNEP (2001) Depleted Uranium in Kosovo. Post-Conflict Environmental Assessment; United Nations Environmental Programme: Nairobi, Kenya: 186 p