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The influence of soil type on maize and wheat uranium uptake

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Abstract

One of the ways that uranium enters the environment is via the use of mineral phosphate fertilisers. A further route of uranium depends on soil properties, grown plants and groundwater. The uranium mobility in soil is regulated by environmental pH, red-ox potential, soil structure and mineral composition of a solid phase. The aim of this research was to define the levels and trends of uranium distribution in three different soil types and organs of grown maize and wheat, due to the long-term application of phosphate fertilisers. Uranium content was determined in plants and soil types. Fresh plants were washed, dried and burned. Final ash was further processed for determination of uranium concentration by fluorescent spectroscopy. The results indicated that the concentrations of uranium in fertilised soils were within its natural limits. Significant differences in uranium content in various parts of maize and wheat were found to be subject to the soil type, which was not the case regarding the nutrition treatment. In the three soil types tested, the results suggested that uranium concentration in soil decreases with an increase in soil acidity, which is in contrast to its accumulation in roots of cultivated plants.

Keywords: maize, phosphate fertilisers, soil types, uranium, wheat

1. Introduction

Maize (*Zea mays*) and wheat (*Triticum aestivum)* are two of the most dominant cultivated plants in Serbia. Serbia has about 3.5 million hectares of agricultural land on which maize and wheat occupy an area of about 1,300,000 and 800,000 ha, respectively (Stanojkovic *et al.*, 2012). In terms of sustainable agriculture, the yield and quality of these cultures are very important and they are primarily affected by the chemical and physical characteristics of soil (Rose *et al.*, 2009).

Long-term fertilisation has a significant influence on the properties of soil including the content of nutritive elements but also on the content of harmful elements like heavy metals and radionuclides (Kratz and Schnug, 2006; Wang *et al.*, 2008).

Uranium is one of the most frequent pollutants of groundwater and surface soil with high radioactive chemical toxicity (Stojanovic *et al.*, 2011). Long-term chronic intakes of uranium through food, water or air can have serious consequences for human health, primarily for the kidneys, liver, and lung, ultimately causing cancer. Inappropriate use of the uranium-contaminated soils may pose significant risks to human health, primarily via the food chain (Duquene *et al.*, 2006).

Previous publications have shown that one of the main sources of soil contamination by uranium in Serbia during the last twenty years was the use of cheap, poor quality and often radiologically unsafe phosphate fertilisers, caused by uncontrolled imports due to limited production capacities (Stojanovic *et al.*, 2006). These, in combination with a lack of the necessary legislation, an adverse economic climate, political sanctions and institutional constraints resulted in a burden with a legacy of environmental degradation, predominantly of land.

Around 1,500 t of phosphate fertilisers was applied annually in Serbia; this represents around 210 kg of uranium (30 g/ha) directly introduced into the environment (Stojanović *et al.*, 2006). The uranium content of phosphate rocks varies according to their geographical origin from 10 up to 360 mg/kg (Kratz *et al.*, 2008). Kratz and Schnug (2006) reported that from 7 up to 23 g/ha uranium (annually) can be released into the soil, using 22 kg/ha of various phosphate fertilisers. Phosphate-based mineral fertilisers distributed in Serbia during 2006 had between 0.3 and 153 mg/kg uranium (Stojanović, 2006). According to Lamas (2005), the natural uranium content of soil varies from 0.1 up to 11.2 mg/kg.

An increase in uranium concentrations as a result of the long-term application of phosphate fertilisers has been reported by several authors (Rothbaum *et al.*, 1979; Schipper, 2011; Taylor, 2007; Tunney *et al.*, 2009). Takeda *et al.* (2006) found at 0-35 cm depth, after a 61-year cultivation period, an increase in the concentration of uranium of 200 mg/m^2. However, Jones (1992) reported no changes in the uranium content of the soil during the 82 years of phosphorus-based fertiliser application. It has been assumed that the loss of uranium over the years could be the result of its leaking from the topsoil, surface soil erosion or plant adoption. Kratz and Schnug (2006) also reported no differences between uranium concentrations in unfertilised and fertilised soil with the triple super-phosphate made from Florida phosphate rock of 65-141 mg/kg uranium. Despite this, Schnug (2005) calculated in his report that slightly more than 1 g/ha uranium could be removed by crop products or by leaching and erosion. Hence, there is no doubt that uranium enters the environment via mineral phosphate fertilisers. However, its subsequent distribution and the risk of its inclusion in the food chain are different for each sample site. The uranium pathway depends on the physical and chemical properties of fertilised soil, groundwater, and the physiological and morphological characteristics of grown plants, and therefore the risk assessment cannot be generalised. Consequently, different opinions regarding this issue emerged.

The literature generally refers to the research conducted on the degree of uranium absorption by different plant species grown under controlled conditions with the addition of uranyl nitrate (Liber *et al.*, 2011; Singh *et al.*, 2005; Stojanović *et al.*, 2010). The mobility of uranium in soil primarily depends on the environmental pH, red-ox potential, soil structure and mineral composition of the solid phase. Pulhani *et al.* (2005) studied the effect of soil fertilisation on the transport of uranium and other radionuclides in wheat. They concluded that the availability of essential nutrients, such as calcium and potassium, regulates the uptake of non-essential elements and that clay mineral and soil amendments strongly affect the uptake, retention and distribution of radionuclides in plants (Pulhani *et al.*, 2005). Rafsanjani (2009) via a pot experiment investigated the uptake of uranium by corn, sunflower and carrot treated with 37 different formulations of phosphorus fertilisers and found statistically significant variations between the nutrition treatments. However, there is still insufficient data in the literature regarding the direct transfer of uranium from fertilised soil to the cultivated plants in real conditions.

The main aim of this research was to determine the levels of uranium accumulation in plant organs of maize and wheat in real conditions, caused by long-term fertilisation, in order to establish the extent to which a soil type alters the uranium uptake by crops and thus potentially threatens the further involvement of uranium in the food chain.

2. Materials and methods

Maize and wheat were grown in three types of soil in Serbia (chernozem, smonitza and pseudoclay). Soils have been continuously fertilised over the past 40 years with an identical fertiliser type each year, containing maximum levels of phosphorus in the formulation. As controls, soil parcels without fertilisation were used. Uranium content was determined in plants and soil.

The experimental fields of the following institutes were used for the investigation: (1) the Institute of Field and Vegetable Crops, RimskiŠančevi, Novi Sad, for soil type chernozem with variant domestic of fertiliser doses $N_{100}P_{100}K_{100}$; (2) Institute for small grain cereals, Kragujevac, for soil type, smonitza with variant of domestic fertiliser doses $N_{120}P_{160}K_{100}$; and (3) the Institute of Soil Science, Topčider, Varna, for soil type pseudoclay with variant of domestic fertiliser doses $N_{150}P_{120}K_{120}$. The subscript indexes of the domestic fertiliser doses indicate the quantity (kg) of elements imported by hectare of soil. Due to a lack of relevant legislation, data on the content of uranium in applied domestic fertilisers were unavailable. The characteristics of the investigated soils are shown in Table 1. Soil samples were composed of ten specimens taken at the different points from the basic parcel. pH values of tested soils ranged between 4.18 and 6.85 with different concentrations of organic matter, clay and dust. Samples for analysis were taken at 0-30 cm depth after harvest.

Plant material was extracted over the three-year period in order to obtain reproducibility of results. During the maturation period, the root, old, young leaves and grains of plants were taken. Young leaves of maize were collected at the stage of 5-7 leaves. Analyses were carried out in five repetitions for each plot.

Table 1. Characteristics of investigated soils.

Type	pH_{KCl}	Organic matter (%)	Clay and dust (%)
Chernozem	6.85	4.68	49.30
Smonitza	5.42	4.45	67.40
Pseudoclay	4.18	1.40	27.90

Fresh plants were washed twice with distilled water, dried at 105 °C and burned at 450 °C. Final ash was dissolved in 12.7 M HNO_3 for determination of uranium. After extraction with 0.1 M trioctylphosphine oxide in ethyl acetate, the intensity of uranium fluorescence was determined with a fluorometer (Thermo-Jarrell Ash Corp., Franklin, MA, USA). The concentration of uranium was determined from standard calibration curves (detection limit 0.005 mg/kg, rang 0.05-5 mg/kg, with correlation coefficient of R>0.997) (Stojanović, 2006). The distribution of uranium in various plant parts was calculated on the basis of dry weight.

Statistical analysis

Statistical analyses were performed using a software package Minitab 16 (Minitab Inc., State College, PA, USA). Normality was assessed with the Anderson-Darling test. Even when no normal distribution of the data transformation (logarithmic, exponential and power) was obtained, data treatment was done with the original data, unless indicated differently. Variations of mean uranium concentrations among the groups (soil type, type of fertilisation and part of the plant) were compared with one and two-way analysis of variance. Significant differences were considered at $P=0.05$ and mean values were ranked by Tukey's multiple range tests, when more than two groups were compared.

3. Results and discussion

The uranium concentrations in soil, roots and leaves of maize and wheat with their standard deviations for all three soil types and both variants of nutrition are given in Table 2. The uranium accumulation in grains of both plants for each analysed condition was below the detection limit (<0.01 mg/kg) (data not shown).

The highest mean value of uranium was found in fertilised chernozem, on which maize was grown (1.71±0.02 mg/kg). The lowest uranium concentration was recorded in unfertilised pseudoclay, for the same plant species (1.20±0.10 mg/kg; Table 2). When considering each soil type separately, the allocation of uranium in both plants deviated from a normal distribution (Anderson-Darling test, $P<0.05$, for each soil type and variant of nutrition).

Statistical analysis of variances showed that long-term fertilisation of soil on which maize and wheat were grown, did not significantly affect the increase in concentrations of uranium in different soil types, although in both cases pseudoclay samples showed generally lower uranium levels than those found in chernozem and smonitza (Figure 1A). Also, no significant differences in uranium distribution were found between mutual parts of both plants, regarding the method of nutrition (two-way ANOVA, F=0.502, $P=0.673$ for maize and F=0.45, $P=0.721$ for wheat; Figure 1B). In contrast to this, the differences in uranium concentrations regarding the part of the plants versus soil type were significant (two-way ANOVA, F=12.84, $P<0.001$ for maize and F=13.86, $P<0.001$ for wheat, respectively).

The roots of maize cultivated on unfertilised and fertilised pseudoclay absorbed significantly higher amounts of uranium in comparison with those grown on chernozem and smonitza (one-way ANOVA, F=37.76, $P=0.007$). The roots of wheat cultivated on unfertilised and fertilised chernozem absorbed a lower quantity of uranium in

Table 2. The mean uranium concentrations (mg/kg) in soil, roots and leaves of maize and wheat with their standard deviations for three soil types and both variants of nutrition (n=5).

Soil type		Soil	Root	Old leaf	Young leaf
		Maize			
Chernozem	unfertilised soil	1.56±0.03	0.32±0.02	0.053±0.001	0.010±0.002
	fertilised soil	1.71±0.20	0.33±0.04	0.050±0.006	0.013±0.004
Smonitza	unfertilised soil	1.46±0.09	0.37±0.02	0.078±0.004	0.018±0.004
	fertilised soil	1.57±0.01	0.35±0.03	0.072±0.010	0.019±0.004
Pseudoclay	unfertilised soil	1.20±0.10	0.46±0.02	0.063±0.004	0.016±0.001
	fertilised soil	1.32±0.07	0.50±0.03	0.069±0.004	0.017±0.002
		Wheat			
Chernozem	unfertilised soil	1.62±0.10	0.39±0.05	0.032±0.003	0.015±0.002
	fertilised soil	1.69±0.09	0.41±0.01	0.028±0.008	0.011±0.008
Smonitza	unfertilised soil	1.58±0.11	0.46±0.02	0.032±0.010	0.016±0.004
	fertilised soil	1.67±0.12	0.49±0.03	0.035±0.012	0.017±0.004
Pseudoclay	unfertilised soil	1.40±0.14	0.52±0.04	0.041±0.004	0.020±0.004
	fertilised soil	1.47±0.10	0.52±0.05	0.035±0.005	0.017±0.003

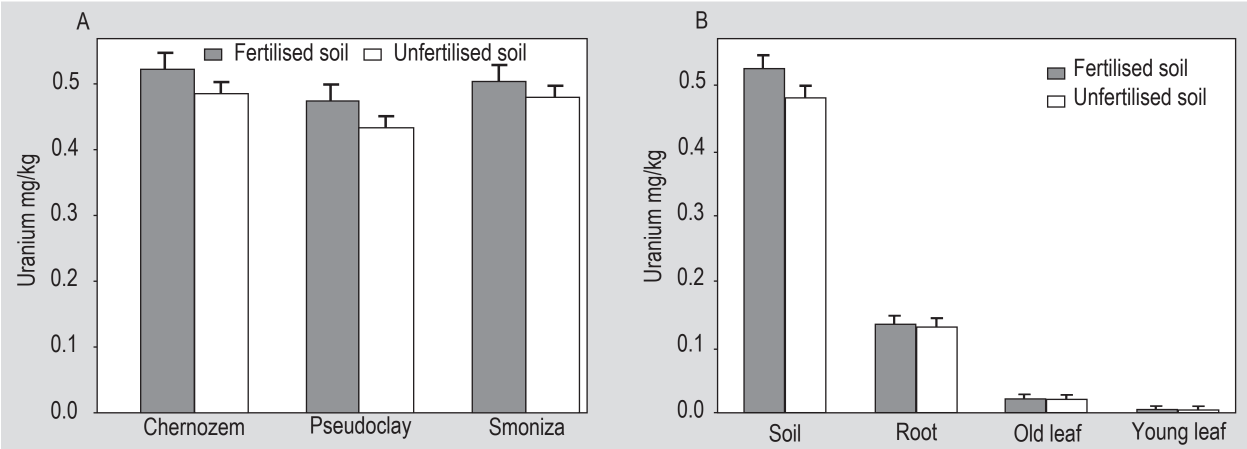

Figure 1. Variations in mean uranium concentrations subject to nutrition treatment (fertilised, unfertilised) versus (A) soil type on which maize was grown, and (B) soil and various parts of maize. In both cases, no significant differences were found. Presented dependences are similar for wheat, which are not shown.

relation to those grown on pseudoclay and smonitza (one-way ANOVA, F=33.95, *P*=0.009; Figure 2). Old leaves of maize accumulated notably different amounts of uranium regarding the soil type (one-way ANOVA, F=22.29, *P*=0.016). Young leaves of maize grown on chernozem showed lower uranium levels versus the same leaves of maize grown on pseudoclay and smonitza (one-way ANOVA, F=18.48, *P*=0.021; Figure 2A). Significant differences were not found between uranium concentrations in old and young leaves of wheat regarding the soil type (Figure 2B).

The variations in uranium uptake by maize and wheat in different soils could be a result of the physical and chemical properties of the tested soils. In the pH range from 6.1 to 7.5, fixation of uranium ions is stable. In such soil conditions the availability of uranium for plant adoption is reduced (Tunney *et al.*, 2009). Stojanović *et al.* (2011) indicated that the soil pH value was the dominant factor that significantly controlled the mobility and availability of uranium, in relation to other soil parameters. Authors also concluded that the reduction in the pH value increases the mobility of uranium and thus its availability for plant uptake. The results obtained here confirm the above, where chernozem with the highest pH of 6.85 showed the highest uranium levels.

On the other hand, acidified soil poor in organic matter, such as the pseudoclay investigated (1.4%) with pH 4.18, favours the acid-soluble forms of uranium, which are more available for plant uptake (Gavrilescu *et al.*, 2009). Butnik and Ishchenko (1990) were among the first authors to deal with this issue. They assumed that the application of fertilisers changes the relative ratio

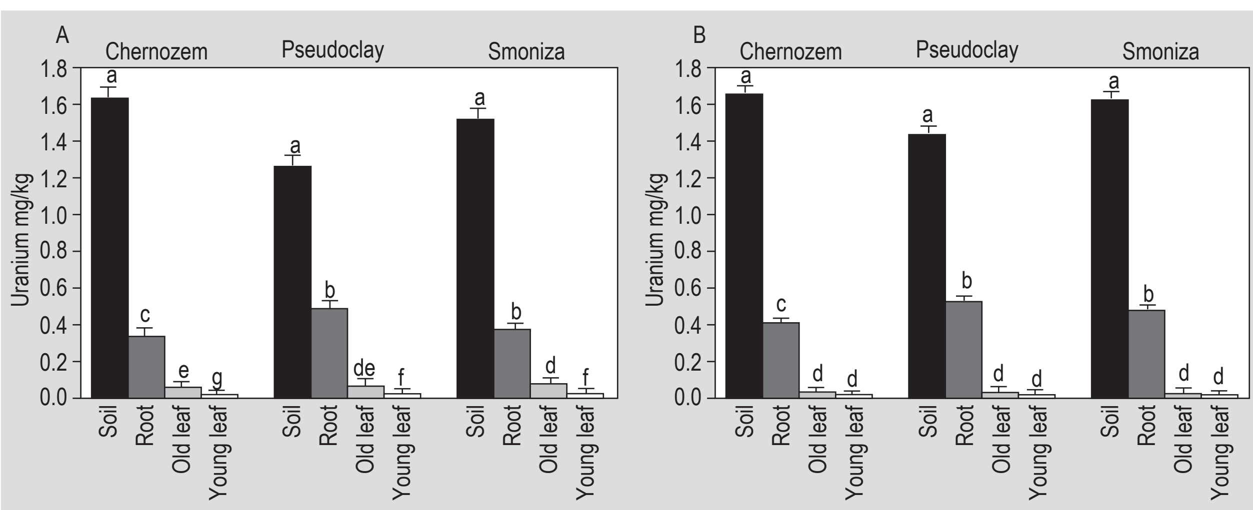

Figure 2. Mean uranium concentrations in soil samples and different parts of (A) maize and (B) wheat in relation to soil type. Means that do not share a letter are significantly different.

of soluble, acid soluble and fixed forms of uranium and that the soil characteristics and the quantity of fertiliser determine what this ratio will be. A possible explanation is that phosphate ions under specific soil conditions affect the transformation of uranium into insoluble forms (Rafsanjani, 2009). It is known from the previous research that the fixation of uranium can be explained by two main mechanisms: precipitation (including oxido-reduction) by soil minerals (clay and dust) and adsorption by the soil organic matter (Yamaguchi *et al.*, 2009). Clay and dust as ion exchangers are able to bind uranyl ions, but not permanently. When equilibrium is established between the clay as solid phase and soil solution, the clay fixes uranium till saturation and an excess of uranium remains in the soil solution. When the concentration of uranium in the soil solution drops, clay becomes the source of uranium until a new equilibrium is established. The high clay content in smonitza (67.40%) and chernozem (49.30%) enables better control of uranium mobility. Chernozem is also characterised by the highest concentration of organic matter (4.68%), which is a major pool for uranium originating from phosphate fertilisers. Chernozem clay minerals, mostly from the group montmorillon with high adsorption capacity, reduce the mobility of uranyl ions, so they form stable low-soluble complexes. These forms of uranium cause its accumulation in the soil surface resulting in reduced availability of uranium to crops. This is important from the environmental protection point of view and for the production of healthy and safe foods.

4. Conclusions

From our studies it can be concluded that the uranium uptake by maize and wheat depends primarily upon the soil characteristics. Soils with pH values above 6 and high levels of organic matter, clay and dust, prevent fertiliser-derived uranium from leaching out to aquifers surrounding agricultural fields, causing the accumulation of its low-soluble forms in the soil surface. In this way, uranium becomes unavailable for plants. This is verified by our findings, where uranium content in soil decreases in the order: chernozem > smonitza > pseudoclay, while the uranium content in roots of maize and wheat decreases in the sequence: pseudoclay >> smonitza > chernozem. Although it is not a biogenic element, uranium accumulates predominantly in the vegetative organs, and then in the generative ones, which in terms of its involvement in the food chain is of major importance. Additionally, the results suggest that the long-term application of phosphoric fertilisers for plant nutrition does not contribute to uranium contamination on the scale of statistically valid differences, irrespective of the soil type on which they are grown. On the other hand, the present study indicates that soil type plays a dominant role in the risk assessment of uranium inclusion in the food chain. Therefore the results presented here are encouraging and allay fears of an existing uranium contamination of crops originating from phosphate fertilisers, minimising concerns about eating a potentially unsafe food.

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