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## Phosphorus fertilizers as a source of uranium in Serbian soils

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**Abstract** – Around 1500 t of mineral fertilizers based on phosphorus are applied per annum in Serbia. It is estimated that around 210 kg of uranium (30 g/ha) are in this way introduced into the environment. Due to this fact there is a risk of exposing local population to ionizing radiation. The purpose of this article was to determine whether long-term application of phosphorus fertilizers causes increase of uranium content in arable soils. These investigations were made using field experiments that were set up on three types of soil, chernozem, smonitza and pseudogley, more than 30 years ago. Same variants of mineral nutrition were used in these experiments and all fields had parcels without application of fertilizers (controls). Soil samples were taken from two soil layers (0–30 cm and 30–60 cm) continuously in a period of five years. Statistical analysis of the results obtained indicates that significant differences exist between the control and application of phosphorus fertilizers in the layer from 0–30 cm, while no such differences were found for the layer from 30–60 cm. Physicochemical soil properties change the process of uranium migration and mobilization. Indeed the fixation of uranium by investigated soil types decreases in the following order: chernozem>smontitza>>pseudogley. Since the natural content of uranium in Serbian soils is in the interval from 0.08 to 5.9 ppm, it can be concluded that the results obtained in this investigation are within natural limits. Indeed, the values obtained for total uranium content in the investigated experimental variants were in the range from 0.65 to 1.94 ppm. This finding is of great value from the aspect of environmental protection and prevention of uranium of anthropogenic origin to be incorporated in food chain.

uranium / phosphorus fertilizers / soils / contamination

### 1. INTRODUCTION

The main anthropogenic source of uranium in the environment is processing of phosphates and application of phosphorus fertilizers. It is estimated that around 21 000 tons of uranium are introduced into the environment annually, and this estimate is based on annual processing of phosphorus ores in the world (around 135 million tons). This represents 73% of total uranium input. According to analyses presented by UNSCEAR (1993), the world's annual requirement of phosphorus fertilizers, estimated at 30 000 000 t P<sub>2</sub>O<sub>5</sub>, leads to an increase in <sup>238</sup>U content of about 1%. Total yield of dose intensity enhancement, through the application period of one hundred years of those fertilizers, is estimated at around 1 nGy/h, which is the minor part of the normal natural soil phon of 60 nGy/g. Some authors (Jones et al., 1992) analyzed samples of surface soil in Morow plots, from continual maize production, with and without addition of superphosphates, in the period 1904–1985 and identified an increase in uranium content in soil samples that were treated with superphosphates. The average increase was reported as 0.74 mg/kg or 26% in relation to untreated soils. Similar investigations in Rothaunted and in New Zealand plots identified an increase in uranium content of 0.45 mg/kg in soil

treated with superphosphates, which accumulated in surface layer soil of 23 cm (Rotbaum et al., 1979).

Around 1500 t of mineral fertilizers based on phosphorus are applied per annum in Serbia. It is estimated that around 210 kg of uranium (30 g/ha) are in this way introduced into the environment. Due to this fact there is a risk of exposing local populations to ionizing radiation (Popović et al., 2001; Donne, 1999). Some authors (Kljajić et al., 1995) estimate that around 85% of the world's phosphate ores have been used to produce mineral fertilizers. Use of 1 000 000 t phosphates with an average value of uranium of 150 ppm (annual production and utilization of mineral fertilizers) leads to 150 t of uranium input into the environment ( $3 \times 10^9$  Bq). The average content of uranium in phosphates is 30–300 mg/kg (Harmstek and De Haan, 1980). Uranium concentration in phosphorus fertilizers is the same as in the raw materials. It is estimated that an annual use of 100 kg P<sub>2</sub>O<sub>5</sub> per hectare (1 kg P<sub>2</sub>O<sub>5</sub> has 100 mg U) will lead to an annual accumulation of 10 g U/ha in soils. This uranium accumulation in the surface layer of soil (20 cm) can cause an increase in uranium content of 3 µg U/kg soil, and it means in 300 years the increase will be 1 mg U/kg soil. Manojlović et al. (1989) did not determine statistically significant differences in uranium content identified in non-fertilized Serbian soils and

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**Table I.** Some specific properties of the investigated soils.

Type of soil	Depth (cm)	pH <sub>KCl</sub>	Organic mat. (%)	Clay and dust (%)
Chernozem	0–30	6.20	4.60	48.30
	30–60	6.35	4.86	50.20
Smonitza	0–30	5.62	4.90	62.40
	30–60	5.20	3.90	72.30
Pseudogley	0–30	4.45	1.30	24.90
	30–60	4.60	1.50	31.00

soils treated with phosphate fertilizers. Serbian factories of mineral fertilizers work with phosphates from Jordan, Morocco, Korea and Togo, with an average uranium content of 50–200 ppm (Harmstek and De Huan, 1980). Around 90% of uranium from phosphates goes into phosphorus acid, and finally into fertilizers. The uranium content in phosphorus fertilizers is 10–150 ppm (Stojanović, 2000). Uranium is in a form of uranyl ion ( $\text{UO}_2^{2+}$ ) with a high level of solubility and mobility in the environmental conditions.

The purpose of this paper was to determine whether long-term application of phosphorus fertilizers causes an increase in uranium content in arable soils in Serbia. Apart from this, the effect of soil depth on the concentration of uranium was investigated.

## 2. MATERIALS AND METHODS

These investigations were made possible thanks to a number of field experiments that were set up on three types of soil (*chernozem*, *smonitza* and *pseudogley*) more than 30 years ago. The same variants of mineral nutrition were used in these experiments, which all had parcels without application of fertilizers (controls). The experimental fields of the following institutes were used for the investigation:

1. Institute of Field and Vegetable Crops-Rimski Sancevi, Novi Sad, soil type *chernozem*. Variant of nutrition:  $\text{N}_{100}\text{P}_{100}\text{K}_{100}$ .
2. Institute for small grain cereals, Kragujevac, soil type *smonitza*. Variant of nutrition:  $\text{N}_{120}\text{P}_{160}\text{K}_{100}$ .
3. Institute of Soil Science – Topcider, Varna, soil type *pseudogley*. Variant of nutrition:  $\text{N}_{150}\text{P}_{120}\text{K}_{120}$  (indexes show the quantity of elements imported per hectare of soil).

Some specific properties of the investigated soils are presented in Table I.

In all these experiments the effect of mineral nutrition on wheat and maize was investigated. Soil samples for uranium analysis were taken from two soil layers (0–30 and 30–60 cm) in 1989, 1990, 1991, 1993, and 1995, after harvesting of wheat and 1990, 1991, 1992, 1993, and 1995, after maize. An average sample of 1 kg is composed of ten single samples of 100 g, taken from different places in the elementary parcel.

Uranium content was determined by the fluorometric method by employing a 26-000 Jarrell Ash Division instrument. The concentration of U was determined from standard U calibration curves (lower detection limit of 0.001 ppm fused

pellet). The results represented are average values of three replications.

The content of total uranium was determined by decomposing 2 g of soil sample with concentrated HF and  $\text{HNO}_3$  acid. The dry residue was dissolved in 8% solution of  $\text{HNO}_3$ . Uranium extraction was obtained with 10-cm<sup>3</sup> synergistic mixtures of 0.1 M TOPO (tri-*n*-octylphosphine oxide) in ethyl acetate. Organic phase aliquots were evaporated until dry and the dry residue was heated to 700 °C with a mixture of NaF (9%) +  $\text{NaKCO}_3$  (91%). Fluorescence intensity was measured with a fluorometer and it is in linear dependency with the uranium concentration (Stojanović et al., 1993).

Available uranium was determined by extracting 10 g of soil sample with 50 cm<sup>3</sup> of  $\text{AcNH}_4$  solution for a period of 2 hours ( $\text{AcNH}_4$  solution: 77 g of  $\text{CH}_3\text{COONH}_4$  and 50 cm<sup>3</sup> of glacial acetic acid in 1000 cm<sup>3</sup>, pH-4.8). Extracted uranium was determined in the same manner as total uranium (Tessier et al., 1979).

Gamma spectrometric analysis was used for analyzing the soil samples – type chernozem, taken in 1995 after maize.

The activity concentration of radionuclides was determined using a high-resolution HPGe  $\gamma$ -spectrometer, “ORTE”, 25% efficiency and 1.85 keV on 1.33 MeV resolution. Samples of the soil were dried at 105 °C, milled and sieved. Every analyzed sample was 500 g. The samples were placed into Marinelli beakers, and after four weeks we carried out gamma spectrometry analysis (Debertin et al., 1988). The analytical data obtained were subjected to statistical analysis (*t*-test and LSD test).

## 3. RESULTS AND DISCUSSION

The results of uranium content in the investigated soils, after maize, for the period 1989–1995, for all three localities (control and treatment) and from two sampling depths are presented in Table II. The results of uranium content in the investigated soils after wheat harvest for the period 1990–1995 are presented in Table III. The observed differences among the uranium contents in control samples taken in different periods are probably the effects of different weather conditions in that area.

We compared (Tab. IV) the average values for soil analysis after maize and wheat for all three locations, control and treatment at two sampling depths. The results were obtained by mean of a *t*-test. The results indicate significant and highly significant differences among pseudogley soils in relation to smonitza and chernozem soils, for both sampling depths and both nutrition treatments. The lowest uranium contents were reported in pseudogley soil types and the highest in chernozem soil types. The same trend is noted for both investigated depths. The differences established result from the physical and chemical properties of the investigated soil types.

Acidified soils, poor in humus such as our pseudogleys, are ideal for the acid-soluble forms of uranium, available for plant adsorption. Such uranium forms migrate downwards in the soil profile up to geochemical barriers, suitable for overturning or fixation of uranium. Therefore, the uranium content in topsoils of pseudogley type is the lowest in relation to the other investigated soils. The smonitza soil type had a higher uranium content in regard to pseudogley and lower in regard to chernozem.

**Table II.** Content of uranium (ppm) in various types of soil, after maize for the period 1989–1995.

Type of soil	Variant of nutrition		1989	1990	1991	1992	1993	1995
C	Control	A	1.06 ± 0.08	1.47 ± 0.13	1.58 ± 0.16	1.78 ± 0.02	1.62 ± 0.06	1.72 ± 0.06
		B	1.26 ± 0.10	1.58 ± 0.08	1.63 ± 0.13	1.76 ± 0.09	1.68 ± 0.09	1.80 ± 0.10
	Treated	A	1.45 ± 0.19	1.76 ± 0.14	1.72 ± 0.20	1.78 ± 0.08	1.72 ± 0.09	1.70 ± 0.08
		B	1.58 ± 0.06	1.76 ± 0.10	1.76 ± 0.06	1.78 ± 0.10	1.78 ± 0.09	1.72 ± 0.06
S	Control	A	1.06 ± 0.18	1.39 ± 0.16	1.61 ± 0.07	1.47 ± 0.05	1.56 ± 0.09	1.37 ± 0.11
		B	1.38 ± 0.10	1.45 ± 0.11	1.65 ± 0.03	1.52 ± 0.06	1.45 ± 0.02	1.61 ± 0.18
	Treated	A	1.41 ± 0.16	1.66 ± 0.16	1.67 ± 0.05	1.33 ± 0.04	1.53 ± 0.08	1.76 ± 0.09
		B	1.29 ± 0.19	1.68 ± 0.04	1.66 ± 0.05	1.61 ± 0.13	1.56 ± 0.11	1.68 ± 0.12
P	Control	A	0.89 ± 0.09	0.81 ± 0.19	1.11 ± 0.13	1.41 ± 0.05	1.41 ± 0.08	1.09 ± 0.20
		B	1.06 ± 0.20	1.10 ± 0.09	1.29 ± 0.07	1.36 ± 0.16	1.56 ± 0.11	1.31 ± 0.19
	Treated	A	0.95 ± 0.10	1.21 ± 0.13	1.26 ± 0.14	1.51 ± 0.03	1.61 ± 0.09	1.26 ± 0.17
		B	1.07 ± 0.12	1.28 ± 0.12	1.24 ± 0.11	1.48 ± 0.10	1.60 ± 0.18	1.36 ± 0.16

(depth A–0–30 cm, depth B–30–60 cm). C-chnozem; S-smonitza; P-pseudogley.

**Table III.** Content of uranium (ppm) in various types of soil after wheat for the period 1990–1995.

Type of soil	Variant of nutrition		1990	1991	1992	1993	1995
C	Control	A	1.59 ± 0.10	1.62 ± 0.09	1.58 ± 0.16	1.62 ± 0.07	1.67 ± 0.06
		B	1.60 ± 0.14	1.56 ± 0.08	1.63 ± 0.13	1.55 ± 0.09	1.46 ± 0.10
	Treated	A	1.65 ± 0.05	1.75 ± 0.11	1.65 ± 0.12	1.66 ± 0.08	1.71 ± 0.01
		B	1.70 ± 0.12	1.68 ± 0.09	1.67 ± 0.06	1.69 ± 0.08	1.71 ± 0.01
S	Control	A	1.59 ± 0.18	1.57 ± 0.04	1.59 ± 0.09	1.65 ± 0.09	1.60 ± 0.15
		B	1.70 ± 0.12	1.53 ± 0.05	1.54 ± 0.16	1.62 ± 0.19	1.56 ± 0.13
	Treated	A	1.72 ± 0.06	1.74 ± 0.08	1.68 ± 0.16	1.67 ± 0.13	1.69 ± 0.17
		B	1.72 ± 0.09	1.68 ± 0.12	1.57 ± 0.13	1.69 ± 0.13	1.59 ± 0.16
P	Control	A	1.28 ± 0.16	1.44 ± 0.10	1.48 ± 0.12	1.63 ± 0.06	1.42 ± 0.09
		B	1.20 ± 0.09	1.32 ± 0.08	1.38 ± 0.10	1.58 ± 0.10	1.27 ± 0.16
	Treated	A	1.44 ± 0.11	1.46 ± 0.11	1.48 ± 0.13	1.63 ± 0.05	1.54 ± 0.13
		B	1.44 ± 0.12	1.33 ± 0.10	1.36 ± 0.10	1.59 ± 0.09	1.44 ± 0.08

(Depth A–0–30 cm, depth B–30–60 cm). C-chnozem; S-smonitza; P-pseudogley.

**Table IV.** Significance of differences for average values for U content (ppm) for three types of soil (controls and treatments) and two depths (after maize).

Type of soil	Variant of nutrition	Average value	Depth 0–30 cm				
Chernozem	Control	1.53 ± 0.08	0.23*	0.41**	0.03	0.12*	0.16
	Treated	1.69 ± 0.10	0.39*	0.57**	0.13	0.28*	–
Smonitza	Control	1.41 ± 0.11	0.11	0.29*	0.15	–	–
	Treated	1.56 ± 0.09	0.26	0.44**	–	–	–
Pseudogley	Control	1.12 ± 0.10	0.22	–	–	–	–
	Treated	1.30 ± 0.10	–	–	–	–	–
Depth 30–60 cm							
Chernozem	Control	1.62 ± 0.09	0.28**	0.34**	0.04	0.11	0.11
	Treated	1.73 ± 0.06	0.39**	0.45**	0.15	0.22**	–
Smonitza	Control	1.51 ± 0.09	0.17**	0.23	0.07	–	–
	Treated	1.58 ± 0.10	0.24**	0.30	–	–	–
Pseudogley	Control	1.28 ± 0.11	0.06**	–	–	–	–
	Treated	1.34 ± 0.09	–	–	–	–	–

Meaning of symbols: \*  $P < 0.05$ , \*\*  $P < 0.01$ .

**Table V.** Significance of differences for average values for U content (ppm), for three (controls and treatments) and two depths (after wheat).

Type of soil	Variant of nutrition	Average value	Depth 0–30 cm				
Chernozem	Control	1.62 ± 0.09	0.11*	0.17*	0.07	0.02	0.7
	Treated	1.69 ± 0.07	0.18*	0.24*	0.00	0.09*	–
Smonitza	Control	1.60 ± 0.09	0.09	0.15*	0.09*	–	–
	Treated	1.69 ± 0.10	0.18	0.24*	–	–	–
Pseudogley	Control	1.45 ± 0.11	0.06	–	–	–	–
	Treated	1.51 ± 0.10	–	–	–	–	–
Depth 30–60 cm							
Chernozem	Control	1.56 ± 0.11	0.13**	0.21**	0.009	0.01	0.13**
	Treated	1.69 ± 0.09	0.26**	0.34**	0.04	0.12**	–
Smonitza	Control	1.57 ± 0.12	0.14**	0.22**	0.08**	–	–
	Treated	1.65 ± 0.12	0.22**	0.30**	–	–	–
Pseudogley	Control	1.35 ± 0.18	0.05	–	–	–	–
	Treated	1.43 ± 0.10	–	–	–	–	–

Meaning of symbols: \*  $P < 0.05$ , \*\*  $P < 0.01$ .

**Table VI.** Effect of phosphorus fertilizer application on content of total and available uranium (ppm) in chernozem (sampling year–1995).

Plant	Variant of nutrition	b	a	$\frac{a * 100(\%)}{b}$
		U (ppm) Total	U (ppm) Available	b
Maize	Control	1.72	0.122 ± 0.007	7.09
	Treated P	1.73	0.126 ± 0.005	7.20
	5%	0.08	0.015	
	LSD			
	1%	0.12	0.026	

Smonitza, from the Kragujevac region, belongs to acid soils with an average clay and dust content of around 70%, while chernozem belongs to the category of neutral soils with a lower content of clay and dust (50%) and higher content of organic substances.

Soils with higher contents of organic substances have strongly bound the uranyl ions, reducing their migration and thereby their availability to plants. The results of soil analyses, performed on samples taken after wheat harvest, from three localities and two sampling depth ranges, for the period between 1990 and 1995 are presented in Table V. The interpretation of the results obtained is given through the analysis of uranium content in soils where maize was used, considering the fact that the results had the same trend.

The content of total and available uranium was analyzed in chernozem soil samples from the Novi Sad locality, taken in 1995, after maize (Tab. VI). On the basis of the results, it can be concluded that phosphorous fertilizers did not contribute to an increase in uranium forms available for plant assimilation, which is invaluable from the aspect of environmental protection, apropos the enclosure of uranium in the food chain.

Indisputable is the fact that the soil type is definitively meritorious for such results. It is known that chernozem, due to its chemical and physical properties, firmly bonds uranium,

regardless of its anthropogenic or geochemical origin, thus reducing its availability for plants. This interpretation is fully supported by the results of gamma-spectrometric analysis of the soil sample, after maize, from the same locality (Novi Sad) and the same sampling year (1995), Table VII.

#### 4. CONCLUSIONS

On the basis of long-term investigations performed on three soils (*smonitza-Kragujevac*, *chernozem-Novi Sad* and *pseudogley-Varna*) the following can be concluded. Statistical analysis of the results indicates that significant differences (at  $P < 0.05$ ) exist between the control samples and soil samples with the application of phosphorus fertilizers in the layer from 0–30 cm, while no such differences were found for the layer from 30–60 cm. Statistically significant differences were not found between the investigated soil layers. There are significant differences in the average uranium content between pseudogley, on one hand, and the other two soil types (chernozem and smonitza) on the other hand. The highest value for uranium content was in chernozem and the lowest in pseudogley. Physicochemical soil properties have an effect on the process of uranium

**Table VII.** Radioactivity concentration of gamma emitters in chernozem soil samples (Bg/kg) after maize, 1995.

Variant nutrition /iteration	$^{238}\text{U}$	$^{235}\text{U}$	$^{226}\text{Ra}$	$^{232}\text{Th}$	$^{137}\text{Cs}$	$^{40}\text{K}$
Control	48 ± 13	3.4 ± 0.1	32 ± 1	42 ± 2	9.2 ± 3	614 ± 10
Treated	51 ± 16	4.2 ± 0.1	36 ± 1	48 ± 3	8.9 ± 2	664 ± 10

migration and mobilization, and for this reason fixation of uranium in the investigated soil types decreases in the following order: *chernozem* > *smonitza* >> *pseudogley*.

The content of available uranium in chernozem soils indicates that there were no statistically significant differences between the control and the variant with the application of phosphorus fertilizer. It can be concluded that phosphorus fertilizers did not contribute to an increase in available forms of uranium. This fact is of great value from the aspect of environmental protection and prevention of uranium (of anthropogenic origin) from being incorporated in the food chain. The natural content of uranium in Serbian soils is in the range from 0.08 to 5.9 ppm, so it can be concluded that the results obtained in this investigation are within the natural limits.

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