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HEAVY METALS, URANIUM AND THORIUM IN AGRICULTURAL SOILS AND PLANTS FROM THE BUHOVO REGION, BULGARIA

Tanja Stoilkova[1], Vasilka Mladenova[1], Dimitrina Dimitrova[2]

[1]*Department of Mineralogy, Petrology and Economic Geology, Faculty of Geology and Geography, Sofia University "St. Kliment Ohridski#", 15 Tsar Osvoboditel Blvd., Sofia 1504, Bulgaria*
[2]*Geological Institute, Bulgarian Academy of Sciences*
Acad. G. Gonchev Str.. bl. 24, 1113 Sofia, Bulgaria
tstoilkova@gea.uni-sofia.bg

A b s t r a c t: Ten soil and five plant samples from private gardens in Buhovo town and from the agricultural area between Buhovo town and Yana village, Bulgaria, were investigated. Inductively coupled plasma mass spectrometry was used for the determination of Cu, Pb, Zn, Cd, Hg, Ni, As, Cr, U and Th concentrations. The results showed higher concentrations of Pb and As in soil samples. The highest contents of U and Th were determined in soils collected from private gardens in Buhovo town and sample collected from the Manastirska riverside. Among the plant samples, the highest uptake of Pb, As, Cr and Cu were established for the sunflower and wheat stems. The comparison of soil and plant samples U/Th ratios clearly indicate uranium enrichment of the sunflower and thorium enrichment of the wheat samples. In the wild briar, hawthorn and reed fruits the contents of U and Th were below the detection limit.

Key words: uranium; heavy metals; soils; plants; Buhovo uranium ore field

INTRODUCTION

Heavy metals are released into the environment by both natural (*naturally occurring radioactive materials* – NORM) and anthropogenic sources (*technologically enhanced naturally occurring radioactive material* – TENORM). Generally, the natural concentration of heavy metals in agricultural soils, derived from soil parent materials, normally is not sufficiently high to harm human health (ATSDR, 2018). However, anthropogenic sources such as mining, waste disposal, urban effluent, sewage sludge, and agrochemicals can greatly increase heavy metal concentrations in agricultural soils (Kabata-Pendias, 2011). The presence of As, Cd, Co, Cu, Pb, Zn, Ni, Hg, U, Th in the environment is of great ecological significance due to their toxicity, translocation through food chains and their non-biodegradability which is responsible for their accumulation in the biosphere (Opaluwa et al., 2012, Rahman et al., 2012, Arogujo et al., 2009). Uranium has both radiotoxicity and chemical toxicity, whereas thorium is to be considered as only radiotoxic.

Uranium mining in Bulgaria started in 1942 at the Buhovo ore field. It is located around 25 km north of Sofia. The ore field was one of the largest uranium mining and processing areas in Bulgaria, covering an area of approximately 70 km^2 until its closure in 1992. The ore was mined underground by means of 7 schafts and 150 mine galleries with total length around 55 km. As a result 198 dumps and tailings ponds with a total volume of 4 Mm^3 rock waste are disposed in the area. The amount of extracted uranium is 4219.4 t (Dikov and Bozhkov, 2014). Two tailings impoundments, covering an area of 100 ha have been constructed near the processing factory. They contain about 5.8 Mm^3 uranium tailing waste which is a complex mixture of waste rock material, radionuclides, Pb, Zn, As, Cu and other heavy metals in the form of sulfates, carbonates, nitrates and complex compounds. Waterproof protection layers were not installed at the bottom of the tailings impoundments at their construction thus some water soluble compounds could seep into the environment (Arhangelova et al., 2010a) .

Only a few studies concerning the contents and the distribution of heavy metals in soils around Buhovo town have been performed. Arhangelova et al. (2010a, 2010b) reported elevated Pb and As concentrations in the meadow soils samples near the Buhovo mine. The values of specific activity of ^{238}U, ^{232}Th and ^{40}K reported to be within the admissible range.

Inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of U and Th contents, ^{238}U/^{232}Th and ^{235}U/^{238}U ratios (Mihaylova et al., 2013). The results showed that the Th and U concentrations in the soils were over 50 times higher than the background values, although the sampling sites were not shown. The U/Th ratio was markedly higher than the control value, suggesting contamination with uranium. The concentrations of U and Th in dandelion, wheat and grass collected near the radioecologically problematic area were found to be higher in comparison with plant samples from unpolluted area.

This study reports the contents of heavy metals, U and Th in agricultural soils and plants in the vicinity of Buhovo town and adjacent reclaimed tailings impoundment.

STUDY AREA

The Buhovo ore field comprises around 10 uranium deposits which are genetically and spatially related to the Buhovo-Seslavtsi pluton and some are hosted in it. Buhovo-Seslavtsi pluton outcrops on the surface as a small (2.5×3 km) stock of monzonite, syenite and quartz-syenite with a gradual transition between them. The syenites and monzonites are cut by dykes of various compositions in the following order of emplacement: syenite-aplite, microsyenites (bostonites) and peralkaline syenite to granite-porphyries (Dyulgerov and Platevoet, 2009). Quaternary materials overlay the primary rocks in the southern part of the studied area.

The host rocks of the uranium deposits are: 1) mainly Silurian argillite and shale with high content of organic matter; 2) rarely – the magmatic rocks; and 3) occasionally – the Ordovician argillite and shale. The tectonic fractures are ore-controlling. The metasomatic ore bodies are stocks, lenses and veins with inconstant uranium content. The main primary mineral is uraninite (pitchblende) associated with other minerals, such as pyrite, chalcopyrite, tennantite, galena, sphalerite, calcite, dolomite and ankerite. Torbernite and autunite occur in the near surface zone. Other rare secondary minerals identified in the deposits are kasolite, soddvite, uranocircite, phosphoruranilite, sabugalite, dewindtite and bessetite (Kalaidjiev, 2009).

MATERIALS AND METHODS

Soil and plant sampling

In September 2015, nine soil samples (S1–7, S9–10) were collected from the upper soil layer (5–25 cm depth) and one sample (S8) was taken from 25 to 40 cm depth according to the ISO 10381-1:2005 and ISO 10381-2:2005. The sampling location of S7, S8 and S9 is from private gardens in Buhovo town where heavy metal industrial contamination is less likely possible. The samples S7 and S8 were taken at one place, but from different depth. The other soil samples were gathered from agricultural areas between the tailings impoundment and Yana village. The weight of each sample was ~1 kg. Five plant samples – wheat stems (P1), reed (*Typha*) stems and leaves (P2), sunflower (*Helianthus annuus*) heads and upper parts of the stems (P3), wild briar (*Rosa canina*) fruits (P4) and hawthorn (*Crataegus monogyna*) fruits (P5) were collected as well. The sampling sites of plants and soils are closely located (Figure 1).

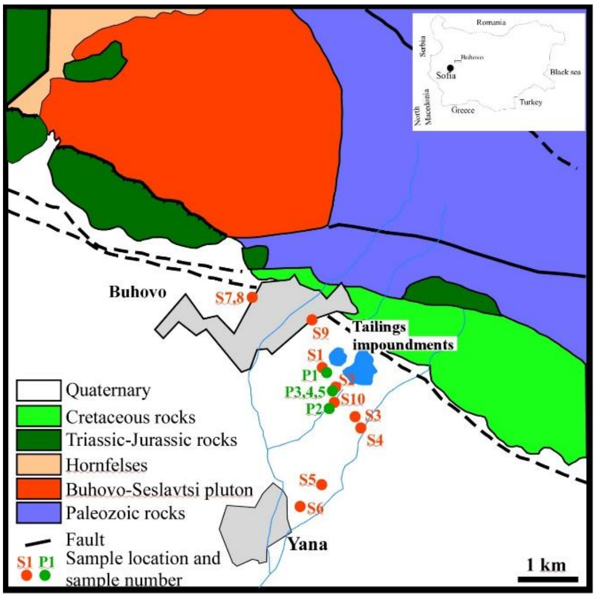

Fig. 1. Simplified sketch map of Buhovo region with sampling points of soils (S) and plants (P) (modified after Angelov, 2010).

Sample preparation

Soil samples. The samples were air-dried, homogenized and sieved. A 3–5 g portions of <0.063 mm fractions were analyzed. The chemical analyses were performed at the Acme Labs – Canada, using ICP-MS in accordance with ISO/IEC-17025:2005.

The soils pH was measured using 1 : 2.5 (wt : wt) ratio of soil sample and deionized water. The mixtures were stored at 25ºC, homogenized five times and pH was measured after 16 h.

Plant samples. The samples were oven-dried at 60ºC for 10 h and milled. After that, 0.5 g of the sample was mixed with 20 ml acid solution (1 : 1 : 1 HNO_3 : HCl : H_2O) and digested in microwave. The analysis was performed using ICP-MS at the Acme Labs.

RESULTS AND DISCUSSION

Heavy metals contents in soils

The measured and the recommended concentration of Cu, Ni, Zn, Pb, Cd, Cr, As, Hg, U, Th as well as the U/Th ratio and pH (slightly acidic to neutral, 6.85 – 7.36) of soil samples are showed in Figure 2 and Table 1.

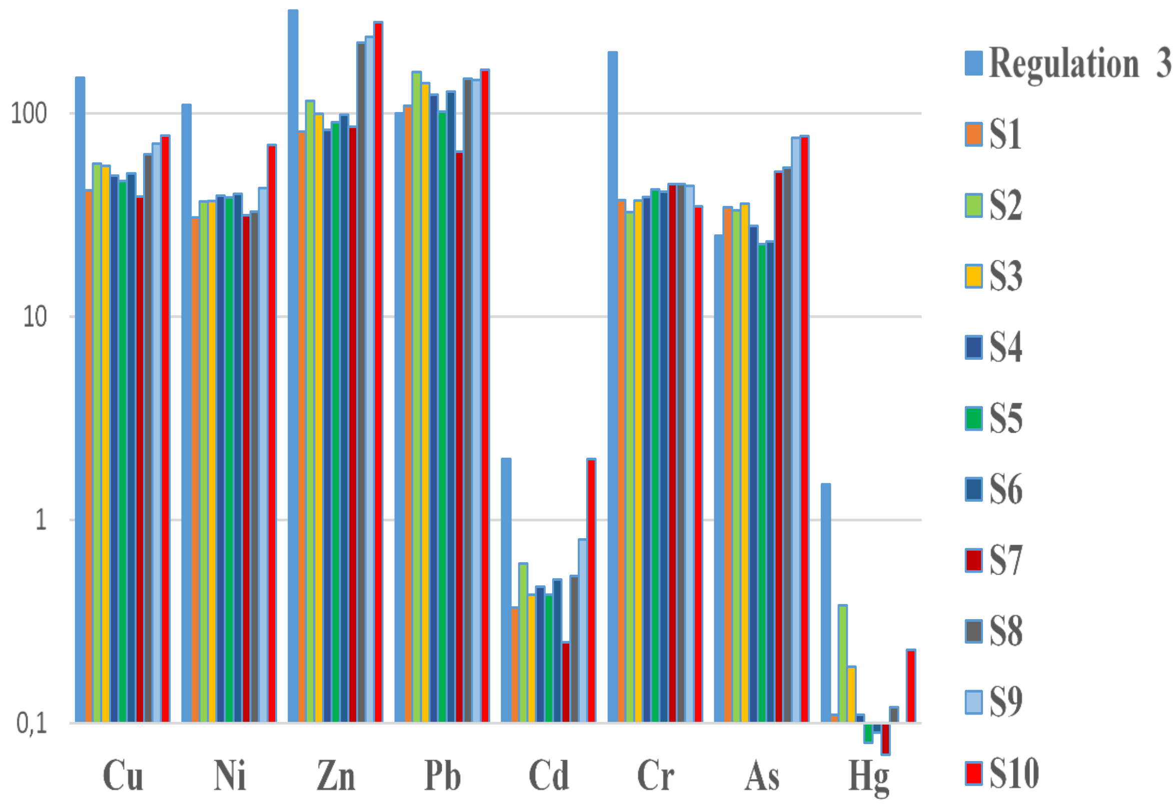

Fig. 2. Heavy metals concentrations (mg/kg) in soil samples

Table 1

pH , U and Th concentrations (mg/kg) in soil samples

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
pH	6.88	6.85	7.02	7.28	7.33	7.40	6.89	7.38	7.3	7.36
U	1.6	1.8	1.2	1.1	0.8	0.7	2.2	2.7	2.6	43.0
Th	7.4	5.6	8.0	7.9	7.5	6.8	25.2	20.8	6.0	7.7
U/Th	0.22	0.32	0.15	0.14	0.11	0.10	0.09	0.13	0.4	5.58

The results showed that the concentrations of Cu, Ni, Zn, Cd, Cr and Hg in all soil samples were below the recommended by the Bulgarian Regulation № 3, 2008 (Figure 2.). The Pb contents in nine samples were higher than recommended levels. Only in S7 soil sample the Pb value was lower – 65 mg/kg. The S10 sample was collected from the Manastirska riverside. Manastirska river drains the Buhovo tailings impoundment and therefore the concentration of all heavy metals and U in S10 sample were higher in comparison to other samples. In the same S10 sample, the highest concentration of Pb (163.7 mg/kg) was detected, which was 1.5 times more than standard value. The analytical results for the As values showed lower levels in S5 and S6 samples. The As concentrations in other soils were two to three times higher than the recommended (Bulgarian Regulation № 3, 2008).

The heavy metals in S7 (surface) and S8 (depth) samples showed increased concentrations of Cu, Pb, Zn, Cd and Hg in the depth. Therefore, the rock forming substrate origin of the heavy metals was assumed (Tomovski et al., 2019, Dyulgerov, 2005). Uranium and thorium contents in uncontaminated soils worldwide vary within the range of 1.9 – 4.4 mg/kg and 8.1 – 11 mg/kg, respectively (Kabata-Pendias, 2011). The highest uranium concentration was measured in sample S10 (43 mg/kg), while the Th content was 7.7 mg/kg (Table 1). The calculated U/Th ratios indicate small variations of 0.09 (S1) to 0.43 mg/kg (S9). Only for the soil sample S10 it was 5.6 mg/kg (Table 1), suggesting contamination with uranium. Additionally, decreasing contents of Zn, As, U and Th from Buhovo town (S7, S8, S9) towards Yana village (S1, S2, S3, S4, S5 and S6) were observed. These higher values in samples from Buhovo town could possibly be due to the participation of Buhovo-Seslavtsi pluton rocks and uranium minerals in the soil formation process as these rocks are enriched in As, U and Th (Dyulgerov, 2005).

In the vicinity of the Yana village Paleozoic and Mesozoic sedimentary rocks containing small quantities of heavy metals have contributed in the soil forming process. Therefore, the concentrations of Cu, Ni, Zn, Pb, Cd, Cr, As, Hg, U and Th in the agricultural soil samples decreased in north-southern direction from Buhovo town to Yana village.

Heavy metals contents in plants

The contents of heavy metals (Cu, Ni, Zn, Pb, Cd, Cr, As, Hg, U, Th) and U/Th ratio in the plant samples are presented in Table 2. The measured concentrations of Pb, As, Cd and Hg were compared to the values listed in Regulation № 10, 2009. Lead and arsenic contents in wheat stem and sunflower heads were higher than recommended, whereas Cd and Hg were within the permissible concentration ranges for all plant samples.

Low levels of Cu, Zn and Cr(III) are essential for humans, animals and plants. They are necessary for maintaining good health of the organisms (ATSDR, 2018). However, high levels, particularly of Cr(VI), can cause harmful effects depending on the dosage, duration of intake and the route of exposure. The highest concentrations of Cr were detected in wheat stems and in sunflower.

T a b l e 2

Heavy metals, U and Th concentrations (mg/kg) in plant samples

	Regulation № 10	P1 wheat steams	P2 reed	P3 sunflower	P4 wild briar	P5 hawthorn
Cu	–	6.56	5.9	20.11	4.38	3.69
Ni	–	6.2	1.6	5.3	0.5	0.7
Zn	–	24	133.5	40	9.1	9.5
Pb	10	10.67	1.12	14.46	0.07	0.25
Cd	1	0.21	0.05	0.24	< 0.01	0.04
Cr	–	13.7	5.3	8.0	1.5	1.5
As	2	2.9	0.2	3.1	< 0.01	< 0.01
Hg	0.1	0.017	0.021	0.039	0.004	0.002
U	–	0.15	0.03	0.22	< 0.01	< 0.01
Th	–	0.9	<0.01	0.37	< 0.01	< 0.01
U/Th	–	0.17	–	0.59	–	–

The highest Zn contents (133.5 mg/kg) was found in reed (stem and leaves). This is probably due to reed's preferential absorption of Zn and the soil substrate, which is probably enriched in Zn, situated near S10 soil sample, showing the highest trace elements content.

The U and Th contents in the wheat and sunflower were considerably higher in comparison to reed, the fruits of wild briar and hawthorn. The wheat and sunflower samples were collected from the places of S1 and S2 soil samples, respectively. The comparison of their U/Th ratios clearly indicate uranium enrichment of the sunflower and thorium enrichment of the wheat samples. According to Kabata–Pendias (2011) the contents of U and Th in the plants vary widely within a broad range and follow their occurrence in soils. Wheat is known to accumulate amounts from 0.0032 to 0.019 mg/kg, whereas sunflower from 0.043 to 0.24 mg/kg. In the wild briar, hawthorn and reed fruits the contents of U and Th were below the detection limit.

CONCLUSIONS

The aim of this research was to provide an assessment of heavy metals contamination in agricultural soil and plants cultivated or grown on these soils. Due to weathering processes all rocks in the area take part in the soil formation.

The lead and arsenic contents in the soil samples were higher than recommended values. The highest concentrations of U, Th and As were measured in soil samples collected from Buhovo town. These soils have been formed close to the uranium deposits related to the Buhovo-Seslavtsi pluton.

The Manastirska River drains the Buhovo tailings impoundment therefore the concentration of all heavy metals and U in the sample from its waterfront were higher compared to the other samples.

The contents of heavy metals, U and Th in the agricultural soil samples decrease in north-southern direction due to the increasing of distance from the uranium deposits.

Among the plant samples sunflower and wheat stems showed higher values of Pb, As, Cr and Cu than recommended. The U/Th ratio showed that the sunflower and wheat were enriched of U and Th, respectively.

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Р е з и м е

ТЕШКИ МЕТАЛИ, УРАНИУМ И ТОРИУМ ВО ПОЧВИТЕ И РАСТЕНИЈАТА ОД ОБЛАСТА НА БУХОВО, БУГАРИЈА

Тања Стоилкова[1], Василка Младенова[1], Димитрина Димитрова[2]

[1]*Оддел за минералогија, петрологија и економска геологија, Геолошко-географски факултет, Софиски Универзитет „Св. Климент Охридски“, Софија 1504, бул. Цар Ослободител 15*
[2]*Геолошки институт, Бугарска академија на науките бул, Акад.Г.Бончев, 24, 1113 Софија, Бугарија*
tstoilkova@gea.uni-sofia.bg

Клучни зборови: ураниум; тешки метали; почви; растенија; ураниумова рудна област Бухово

Испитувани се 10 примероци почва и 5 примероци растенија земени од приватни градини во градот Бухово и од земјоделски површини помеѓу градот Бухово и селото Јана, Бугарија. За определување на концентрацијата на Cu, Pb, Zn, Cd, Hg, Ni, As, Cr, U и Th беше користена масена спектрометрија со индуктивно спрегната плазма (ICP-MS). Резултатите покажаа повисоки концентрации на Pb и As во примероците почва. Висока содржина на U и Th беше утврдена во примероците на почва од приватни градини од градот Бухово и од брегот на Манастирска Река. Кај растенијата висока содржина на Pb, As, Cr и Cu беше удврдена во примероците сончоглед и во стеблото на пченица. Споредбата на односот U/Th во примероците на почвата и на растенијата јасно покажа збогатување со ураниум во сончогледот и со ториум во пченицата. Содржината на U и Th во шипки и во плодовите на глог и трска беше под границите на детекција..