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Uranium content in Technosols formed on naturally loaded proluvial sediments

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Abstract. The content of uranium 238 (^{238}U) in naturally evolved soils with a meta-morphic and poorly developed profile, later technogenically contaminated by the activity of the former "Kremikovtsi" metallurgical plant, located at the foot of the Buhov uranium ore field, was investigated. A total of six soil profiles were analyzed, incl. five from the industrial site of the combine and one control. Data on uranium content were obtained by two methods - Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), simultaneously with results for over 50 chemical elements, as well as measured by its daughter product - thorium 234 (^{234}Th), determined by gamma spectrometric analysis via multichannel analyzer with high purity germanium detector (HPGe). The results demonstrate that the uranium content of the investigated profiles in single cases exceeds the background norms of 11-173 Bq/kg and is within the range of 50±5 - 180±40 Bq/kg. The maximum values of the studied element are obtained from the coarsest profiles, with the maximum content of coarse sand, which suggests a primary state of uranium in the form of ore minerals or isomorphically included in primary insoluble accessory minerals in the soil of the studied profiles. From the research, the characteristic relationship of the heavy metal with the soil organic matter was not established. Still, an accumulation was observed in the cambic horizons of the metamorphic profiles. A factor for the upward migration and accumulation of uranium is the change of the water-air soil regime and establishment of periodic reducing conditions; as a general conclusion, the natural radionuclide undergoes migration from the surface horizons of the studied Technosols.

Key words: evolved soils, poorly developed profile, technogenic contamination, ^{238}U, laser ablation, gamma spectrometry.

Introduction

Natural uranium radionuclides, ^{238}U and ^{235}U, and their decay products pose a significant threat to soil health because of their highly toxic nature. These radionuclides are derived in the soil by weathering of bedrock. The mobility of uranium along these processes depends on the essential minerals. Uranium in persistent minerals such as monazite and zircon can be retained in the soil profile (Kostov, 1993). Conversely, uranyl (UO^{2+}) is from uranium minerals that do not withstand weathering and can be gradually removed by dissolution from rock/soil profiles (Raikov, 1978). However, dissolved uranium may remain in the soil due to the formation of stable hydrolysates, organic complexes or co-precipitation with various compounds such as iron oxides, carbonates, phosphates, vanadates and arsenates. The affinity of uranium to be absorbed by organic matter and concentrated by microorganisms may explain why it often accumulates in coal and peat (Arbuzov et al., 2011). Plants rarely accumulate uranium from the soil because uranium has no known biological function (Aide, 2018).

This study provides preliminary data on the levels of ^{238}U in soil profiles in the former metallurgical combine "Kremikovtsi", Bulgaria. The environment in this region has been subject to harmful impacts for centuries (Pushkarov, 1913), including deforestation and uranium mining, which have led to soil contamination with uranium. The plant, which ceased operations in 2009, is responsible for pollution in the area by emitting harmful gases, and particulate volatile pollutants through the wind have been deposited on the soil (Faitondjiev et al., 2000; Kachova and Ferezliev, 2018; Stoykova, 2021).

On the nearby mountain slopes, there are two deposits: Barite - Iron ore deposit in Kremikovtsi and Buhovo uranium deposit. Exploiting uranium ore in Buhovo has generated piles that have also caused some environmental impacts (Petrova and Tsvetkova, 2020). Groundwaters with acid reactions are the cause of eroded deluvial and proluvial material. The local radionuclide geochemical background is also influenced by Potassium-alkaline Buhovo-Seslavtzi Pluton, which due to its genesis, is naturally enriched in heavy alkali and alkaline earth metals (Ba, Sr, Rb, Cs) and elements with high ionic potential (Th, U, Nb, Ta, Y, Zr, Hf, Ga) (Dyulgerov, 2005). According to Dyulgerov (2005), the uranium content in this magmatic body is very high - 10-40 g/t (ppm). All these factors have induced complexed changes in soils over a long period, resulting in Technosols with a wide area of degraded land, gradually technogenic alkalizing and losing its soil colloids and natural microbiome (Damyanov, 1995; Ecoengeneering - RM, 2017; Stoykova, 2020)

The Buhovo deposit contains predominantly uranyl phosphates - torbernite $Cu[(UO_2)(PO_4)]_2 \times 12H_2O$ and autunite $Ca(UO_2)_2(PO_4)_2 \times 10\text{-}20H_2O$. However, the correlation between uranium, copper, and calcium has yet to be established, according to Stoykova's study (2021). Other uranyl phosphates and uranyl silicates, such as kasolite, soddyite, uranocircite, dewindtite, bassetite and sabugalite are in smaller quantities. Uranium is also present in poorly structured oxides with a transition composition known as pitchblende (UO_2-U_3O_8), associated with Mo. Along with them there are sulfides of Fe, Cu, Zn, Pb, Ni, Co and nickel, iron and copper arsenides such as nickelin NiAs, rammelsbergite $NiAs_2$, tennantite $Cu_{12}As_4S_{13}$, arsenopyrite FeAsS, etc. Due to the ore substance concentration, the general geochemical background has high levels of As, Sb, S, Co, Ni, Zn, P, Mo, etc. (Kalaydzhiev, 1993; Stoykova and Teoharov, 2022).

The study aims to analyze the dispersion, movement and accumulation of uranium in highly contaminated soil profiles from the territory of the former "Kremikovtsi" plant. The study will use mass and gamma spectrometric analysis to present a correlation relationship with a high confidence level for uranium levels.

Materials and Methods

The study was conducted using representative depth profiles ranging between 210 and 400 cm, in accordance with the Guidelines for Soil Description (Jahn et al., 2006). The profiles studied are displayed on a georeferenced map of the former Kremikovtzi territory and the adjacent area (Fig. 1).

Figure 1 illustrates all profiles included in the doctoral thesis on the characterization of soils with geochemical and technogenic loads, formed on Old Quaternary sediments (Stoykova, 2021). This publication focuses on five primary profiles (profiles 3, 6, 7, 8, and 11) and one control profile -13 (k).

Table 1 characterizes the methodical scheme for setting soil profiles, including their geographical position, soil-forming materials, and their relation to various metallurgical productions on the territory of the combine.

The sample preparation for analysis was conducted in accordance with ISO 11464:2012. The publication contains information on the following soil parameters: pH determined using a potentiometric glass electrode in accordance with ISO 10390:2021; texture-determining fractions of soils were determined using Kaczynski's method (1958); the content of soil organic matter was determined by wet burning and titrimetric analysis (Filcheva, 2007).

Data on uranium content were obtained using two methods - Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), simultaneously with results for over 50 chemical elements, as well as measured by its daughter product - thorium 234 (^{234}Th), determined by gamma spectrometric analysis via multichannel analyzer with a high purity germanium detector (HPGe).

The data was presented with descriptive statistics, correlation analysis, and graphical visualization through Microsoft Office Excel software for Windows OS.

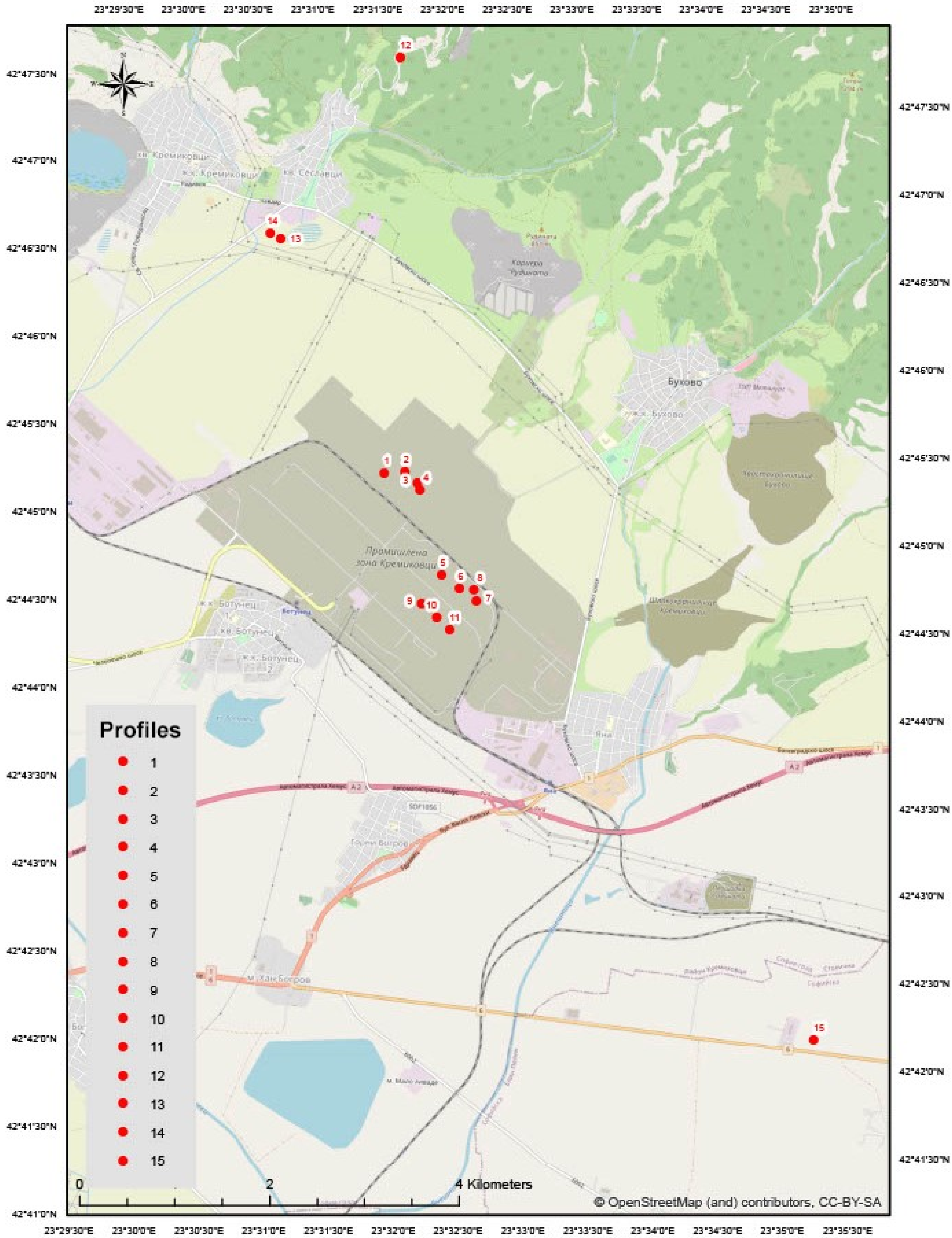

Fig. 1. The situated profiles in the MC "Kremikovtsi" region (Bulgaria) and its vicinity.

Table 1. Grouping of soil profiles studied according to geographical position, soil-forming materials and relationship with the type of production.

Geographical position I	Geographical position II	Geographical position III	Geographical position IV
Pleistocene proluvial sediments	Pleistocene-Holocene sediments	Pleistocene colluvial-provial sediments	Pleistocene colluvial-provial sediments
		Contamination by agglomerate dust from ore production	Contamination with waste from cast iron production – brittle cast iron, coke, undissolved ore, slag, quartz sand
Profile 13(k)	Profile 3	Profile 6, Profile 7, Profile 8	Profile 11

Results and Discussion

Fig. 2 visualizes the ^{238}U content of the soil profiles. The ^{238}U content of soil profiles ranges from 4.5 to 15.3 ppm, an average of 9.9 ppm, three times greater than the geochemical background according to literature data (Kabata-Pendias, 2011). Profile 13k has the lowest ^{238}U content, while profile 6 has the highest; the uranium concentration increases in the following order: profile 13k < profile 11 < profile 7 < profile 8 < profile 3 < profile 6. The control profile (13k), located further away in the northwest direction, has the lowest values for the metal. This may be due to its geographical location, the more advanced evolution of the soil and the likely presence of micro-organisms that influence the physicochemical environment of the soil. Vegetation around the other profiles is scarce, and microbiological analyses revealed a lack of a vital soil microbiome (Stoykova, 2021).

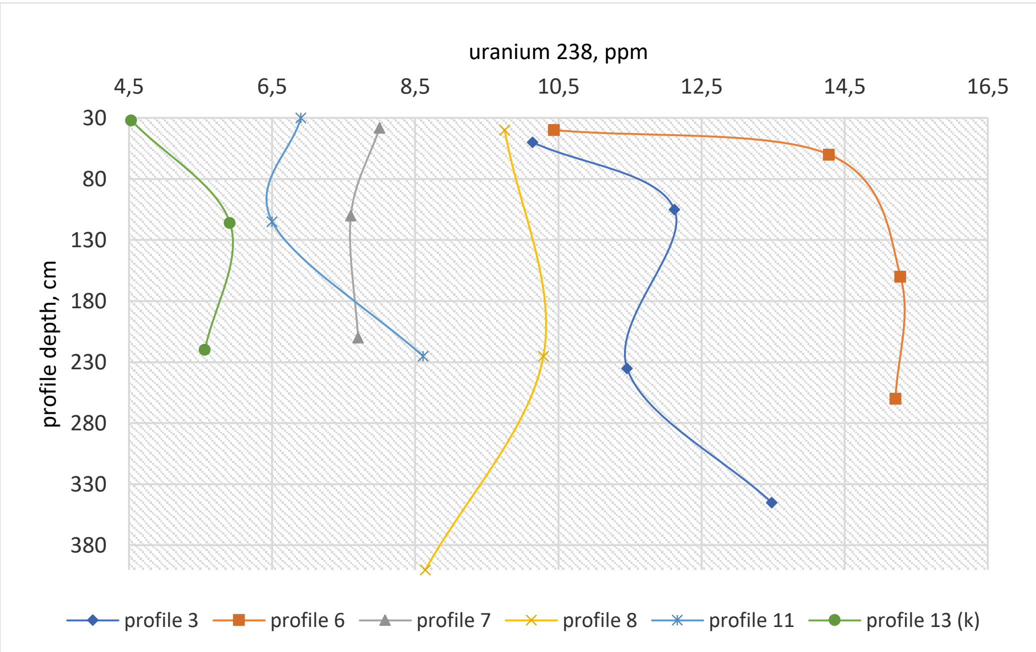

Fig. 2. Distribution of ^{238}U by the depth of soil profiles.

The concentration of ^{238}U on the metallurgical plant's territory is higher than the control area and can hardly be associated with various productions housed there. It is more likely due to the geological materials forming the soil profiles. The presence of uranium ores in the adjacent mountain slopes contributes to the relatively higher values observed in the study.

The levels of uranium in the soil profiles studied by us are influenced by natural geochemical and soil-forming processes that determine the genetic character and development of the soil. As a result, we identified two primary types of soil profiles: Cambisols and Regosols (IUSS Working Group WRB, 2015; Teoharov et al., 2019), whose nomenclature has recently been changed to Technosols due to the toxic levels of metalloids and heavy metals in them (Stoykova, 2021). Profiles 3, 7 and 13k belong to Cambisols, while profiles 6, 8 and 11 are classified as Regosols. In simple terms, the uranium content is higher in the layered structure soil profiles (Regosols), while well-formed genetic profiles (Cambisols) have lower levels of uranium. This is also an indicator of the technogenesis level in each soil profile.

Soil profiles differ in their granulometry. They comprise the sediments of the Old Quaternary Age, representing alternating gravel, sand and clay layers. The sand fraction forms most of the mechanical fractions, accounting for 41.6±2.5%, followed by silt at 23.9±1.6% and clay at 19.5±2.7%. On average, the skeletal fraction of particles > 1 mm was 14.1±2.4%.

Based on the analysis in Fig.3, the soil profiles' uranium content and mineral fractions have been thoroughly investigated. Profile 6 has the highest concentration of uranium and the highest % of coarse sand. This finding helps the theory that a significant amount of radionuclide exists in its original state as uranyl phosphate ore minerals or isomorphically included in primary insoluble accessory minerals in this profile. Furthermore, the correlation analysis showed a positive correlation between uranium and the amount of sand present (r = 0.44), while an inverse relationship exists between the uranium and the clay fraction (r = -0.61).

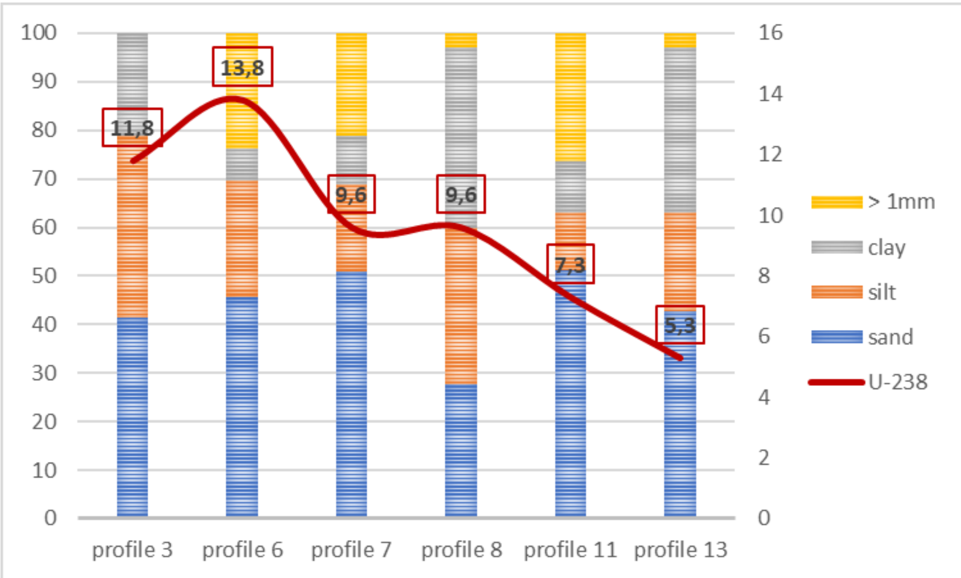

Fig.3. Relationship between average ^{238}U content of soil profiles and % distribution of their mineral fractions

The correlation analysis indicates the relationship between phosphorus, arsenic, vanadium and uranium. It is confirmed by studies showing that uranium ions are adsorbed and form seconddary phosphates, arsenates and vanadates, which are difficult to dissolve (Kabata-Pendias and Szteke, 2015).

Soil-forming rocks consist mainly of Pleistocene proluvial materials, which contain various minerals such as limestones, aleurolites, argilites, lidites, phyllites, syenite and ore substances such as uranium phosphates accompanying sulfides and other heavy metal-containing minerals.

Uranium is an element strongly absorbed by iron and manganese oxides (Salminen et al., 2006). This can lead to the formation of difficult-to-dissolve salts and other elements such as Mo, Co, Ni, Cu, Zn, Cd, As, Pb and ^{232}Th. Research has shown a remarkable positive relationship between uranium and P, Co, Ni, Mo (r = 0.67) and As (r = 0.66), suggesting a genetic relationship with uranium ores. Uranium is an amphoteric metal with a positive charge in an acidic environment and usually crystallizes on soil colloids with a negative charge, such as clays and manganese oxides. There is a significant correlation between uranium and manganese (r = 0.50).

The radionuclide is concentrated in organic soil substances (Roivainen et al., 2011), but it has yet to be established in technogenic profiles because the amount of organic substance is minimal.

In the uncontaminated soil control profile of Rhodic Cambisol, the maximum metal content is found in the cambic horizon of this profile, where weakly alkaline reactions and oxidative conditions exist. The metal is mainly present as primary minerals or various negatively charged complexes adsorbed by positively charged soil colloids, predominantly iron hydroxides. Further research is needed to confirm the relationship between radionuclides and organic substances.

A significant positive correlation between uranium obtained by mass spectrometry and gamma spectrometric methods is shown in the accompanying Figure 4.

The derivation of a correlation relationship between two uranium studies is a significant scientific contribution because theoretical data for the other are obtained in analytical determination by one method.

An assessment of uranium levels determined by gamma-spectrometric analysis against limit values shows that the upper limits sometimes exceed background limits. Uranium is in the range between 50±5 to 180±40 Bq/kg. This can be attributed to the natural geological features of the study area, which is situated on old Quaternary proluvial materials loaded with chemical elements associated with the potassium alkaline Buhovo-Seslavtsi pluton and the Buhov uranium ore field.

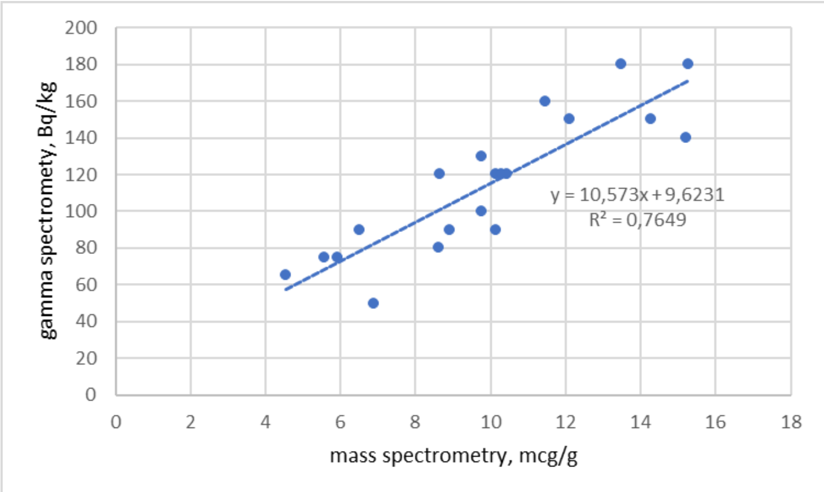

Fig. 4. Correlation between the ^{238}U content obtained by two different methods

Conclusions

Our research has revealed that certain profiles we examined contained uranium levels that exceeded the approved background rates of 11-173 Bq/kg. Specifically, the uranium content ranged from 50±5 to 180±40 Bq/kg, with the highest concentration appearing in profiles that had a high proportion of coarse sand. This finding suggests that uranium may be present as ore minerals or isomorphically included in primary insoluble accessory minerals in these profiles. Although we did not identify a clear correlation between heavy metal and organic matter, we observed accumulation in the metamorphic profiles' cambic horizons. Our research has shown that the movement and buildup of uranium in soil can be impacted by fluctuations in the water-air balance within the soil. This can result in varying conditions for the Technosols we have examined, which may facilitate the movement of uranium from the uppermost soil layers.

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