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ARSENIC CONTENT AND MOBILITY IN AGRICULTURAL SOILS IN TWO POLLUTED AREAS IN KOSOVO

SUMMARY

Arsenic is a toxic chemical that can be found naturally in soil and rock. Exposure to high levels of arsenic in soil can have detrimental effects on human health, including cancer and skin damage. The presence of arsenic in the soil can be caused by both natural and human-made sources, such as mining and industrial activities. A total of 60 soil samples were collected in the agricultural soils of two regions of Kosovo known for pollution with heavy metals. Arsenic was extracted from the soil with aqua-regia (pseudo total concentration), NH_4OAc-EDTA (potential bioavailable), and NH_4NO_3 (mobile fraction). The pseudo total content of As showed a high value in Mitrovice up to 654.89 mg kg^{-1} with a mean of 66.51 mg kg^{-1}, whereas in Drenas region up to 23.63 mg kg^{-1} with a mean of 12.31 mg kg^{-1}. All samples analyzed in the area of Drenas were within the target values, while those of Mitrovica only 50% were within the target values, 30% within the accepted values and 20% above the values allowed for the content of arsenic according to the legislation. The rate of extraction of the potentially bioavailable and mobile form was low with a mean of 0.003 mg kg^{-1} in Drenas area and 0.2683 mg kg^{-1}, respectively 0.008 mg kg^{-1} in the Mitrovica area. The T test showed significant differences between regions in the three forms of arsenic content in agricultural soils.

Keywords: Potential bioavailable, mobile fraction, pollution, target values

INTRODUCTION

Arsenic is a naturally occurring toxic metalloid that is widely distributed in the environment. It can be found in soil, water, and air. Arsenic is often found in ores of silver, tin, lead, cobalt, copper and nickel (Krivokapić, 2020). In

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agricultural soils, arsenic can come from natural sources, such as weathering of mineral deposits, or from anthropogenic sources, such as the use of arsenic-containing pesticides and fertilizers (De Francisco *et al.*, 2021; Singh and Srivastava, 2020; Yamamura and Amachi, 2014). In the USA, herbicides with Arsenic are allowed with strict rules, while in EU countries pesticides based on As are prohibited. Arsenic in agricultural soil can pose a threat to human health and the environment if it is taken up by crops and enters the food chain (He *et al.*, 2021).

Studies have shown that arsenic can accumulate in the roots, stems, and leaves of crops grown in contaminated soil (Cao *et al*., 2019). The extent of arsenic uptake by crops is dependent on various factors such as the chemical form of arsenic in the soil, soil pH, and the type of crop. The process of arsenic (As) uptake by plants from the soil is influenced by several factors, including the chemical forms of arsenic present in the soil, the specific plant species, and the overall concentration of arsenic in the soil. Generally, higher total soil arsenic concentrations lead to increased arsenic uptake by crops (Punshon *et al*., 2017).

Arsenic in agricultural soil can also affect the health of soil microorganisms and invertebrates, which play an important role in soil fertility and nutrient cycling (De Francisco *et al*., 2021). Arsenic toxicity can also lead to reduced growth and productivity of crops (Beniwal *et al.*, 2023), which can have significant economic consequences for farmers.

One of the major sources of heavy metals in Kosovo is the Trepça mine, which has been in operation for over 100 years. The mine produces a variety of minerals, including lead, zinc, and cadmium, which can contaminate the surrounding environment if not properly managed. Industrial activity and mining mostly cause pollution of the agricultural soils and environment, which are located in different parts of Kosovo. Zogaj *et al*. (2014) identified some hotspots in agricultural soils, e.g. field sites near the ore-metallurgic combine “Trepça” in Mitrovice, the ferronickel production plant “Ferronikeli” in Drenas, the battery Factory Ni-Cd in Gjilan and the mine of Kizhnica.

The management of arsenic in agricultural soil is a complex issue and requires a multi-disciplinary approach and in Kosovo there is insufficient investigation about arsenic and their suitability, especially in agricultural soils. It is important to understand the levels of arsenic in soil and take appropriate measures to minimize exposure to this toxic substance. Therefore, the aim of this research is to will provide an overview of arsenic and its mobility in potentially contaminated soils area in Kosovo.

MATERIAL AND METHODS

Study area

The areas of agricultural soils chosen for this study belong to the area of Mitrovica and Drenas, which are considered the most contaminated areas in Kosovo (Zogaj *et al.,* 2014; Maxhuni *et al*.,2023). The area of Mitrovica is located in the northern part of Kosovo and was one of the main industrial sites of

Former Yugoslavia and one of the most important mining districts in Europe (Nannoni *et al.*, 2011). Mitrovice Industrial Park (Trepca) included approximatly 40 mines, various concentrators, flotation and smelting plants, and several factories. This area has begun to be exploited intensively for the production of Pb, Zn, Au, Ag, and Bi from the 1930s, generating various categories of waste. Whereas the area of Drenas is located in the central part of Kosovo and the main industry is Ferronikeli factory, which is very close to agricultural and residential areas. Around 3 million tons of granulated slag is stored in a dump close to the factory.

Soil sampling and analysis

As shown in Figure 1., through the agricultural soils, 30 soil samples were taken per region (60 samples in total) at the plow layer, respectively 0-30 cm depth, according to the random method (BBodSchV, 1999; Theocharopoulos *et al.*, 2001). The soil samples were air-dried and then crushed and sifted to a size less than 2mm. Soil samples were kept at room temperature until analyzed. Soil pH was measured using a $CaCl_2$ solution with a ratio of 1:2.5 (DIN ISO 10390 2005). The total amount of carbon (C) and nitrogen (N) was determined using a C-N-S element analyzer (Elementar) based on gas chromatography. The particle size distribution was obtained by a combination of sieving and pipette methods after the removal of carbonates (HCl) and organic matter (H2O2) and dispersion in Na-pyrophosphate (ISO 14688 – 1: 2003-01 2003).

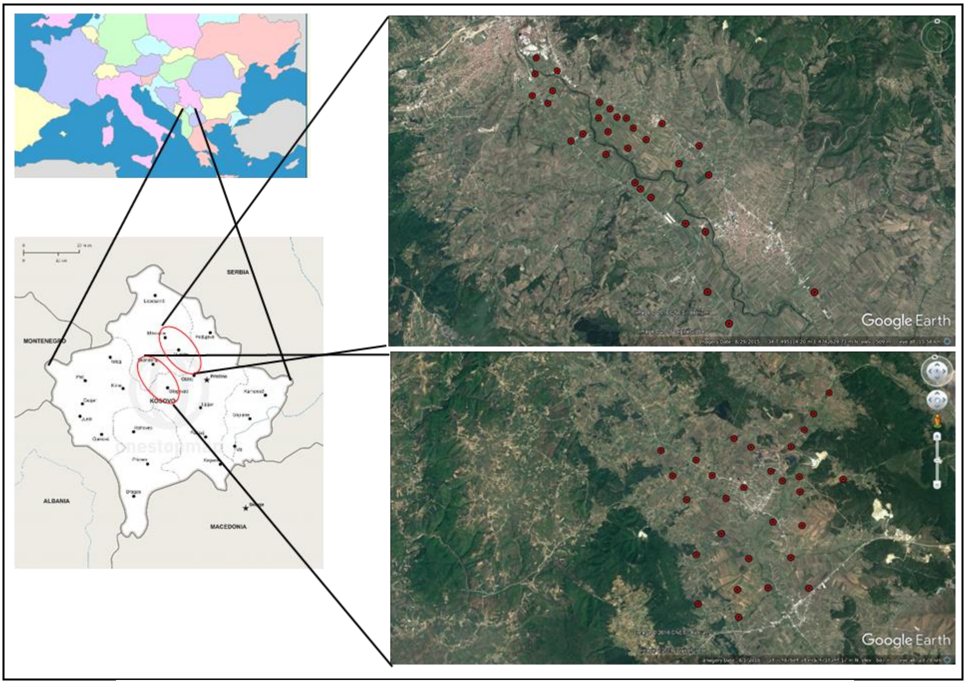


Figure 1. Location and soil sampling sites in the research areas

The method used to extract the pseudo total arsenic contents in soil involved the use of microwave assisted extraction (MAE) with aqua regia (a mixture of 35% hydrochloric acid and 65% nitric acid) from finely ground soil samples, in accordance with the US EPA 3051A method. However, this pseudo total content alone is insufficient to determine ecotoxicologically relevant arsenic. Thus, the exchangeable and mobile fractions of arsenic, which are potentially plant available and easily leachable, were extracted using NH4OAc-EDTA (ammonium acetate and ethylenediaminetetraacetic acid) and 1M NH4NO3, respectively, according to German regulation (DIN 19730:2009).

The arsenic concentrations in soil extracts were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES), the Varian 720ES model.

RESULTS AND DISCUSSION

The study involved the analysis of soil samples to investigate the factors affecting the behavior of arsenic in soil, specifically pH, clay, and carbon (C) content. The impact of two regions on the analyzed parameters was assessed using the Student t-test. Descriptive statistics indicated that the mean pH and clay content were similar between the two regions. However, the mean C content differed significantly between the regions (2.3 and 1.6), as confirmed by highly significant differences in the Student t-test ($p<0.001$) (table 1).

Table 1. The arsenic fraction content and other agricultural soils properties in samples analyzed (n=60)

		Mean	Median	STDEV	Min	Max	T-test
As_{-AR}	*Drenas*	12.31	11.74	3.23	8.37	23.63	-2.448**
(mg.kg^{-1})	*Mitrovica*	66.51	29.88	121.22	11.43	654.89	
As_{-EDTA}	*Drenas*	0.003	0.000	0.006	0.000	0.025	-2.196**
(mg.kg^{-1})	*Mitrovica*	0.268	0.031	0.662	0.000	3.538	
As_{-AN}	*Drenas*	0.003	0.003	0.003	0.000	0.014	-1.86*
(mg.kg^{-1})	*Mitrovica*	0.008	0.004	0.011	0.000	0.063	
pH	*Drenas*	6.07	6.09	0.73	4.54	7.38	0.955^{ns}
	Mitrovica	5.91	5.88	0.54	4.78	6.97	
Clay (%)	*Drenas*	38.03	35.06	12.97	17.22	68.45	-0.020^{ns}
	Mitrovica	38.09	37.78	8.4	22.55	57.28	
C (%)	*Drenas*	2.33	1.91	1.07	1.11	5.04	3.558***
	Mitrovica	1.61	1.6	0.28	1.18	2.22	

Limited value of soil contamination (As): A=30; B=55 and C=80 *mg.kg^{-1}*

*As-AR – Aqua regia extraction; As-EDTA – EDTA extraction; As-AN - Aminium nitrat extraction; ns - no significant difference; *, **, and *** indicate significant differences at 5, 1, and 0.1% confidence level, respectively. A=clean; B=acceptable contamination, but further investigation are required; C=high contamination and needs to be cleaned*
Pseudototal of arsenic in soil

The pseudototal of arsenic content in soil as shown in Table 1, in the Drenas area vary from 8.37 to 23.63 mg kg^{-1}, with a mean of 12.31 mg kg^{-1}. Whereas in the Mitrovica region the content of arsenic was highest with a maximum of 654.89 mg kg^{-1} and minimum 11.43 mg kg^{-1} (mean 66.51). Based on the Kosovo standard (Administrative instruction, 2018) for the level of heavy metals in the soil (the critical value for As 80 mg kg^{-1}), the results have shown that in the region of Mitrovica, 20% of the analyzed samples are above the permitted level or high contamination and needs to be cleaned these soils. Meanwhile, in the Drenas region, all analyzed samples were below the target level according to the Kosovo standard (30 mg kg^{-1}).

There is little data on the content of arsenic in the soils of the Drenas region, especially in agricultural soils, however, according to Imeri *et al*. (2019), in agricultural soils close to industry, the arsenic content was very low, only 0.007±0.001 mg·kg^{-1}. Our results have shown that the content of arsenic is significantly higher, this is probably due to the more advanced technique that we have used for the analysis of soil samples.

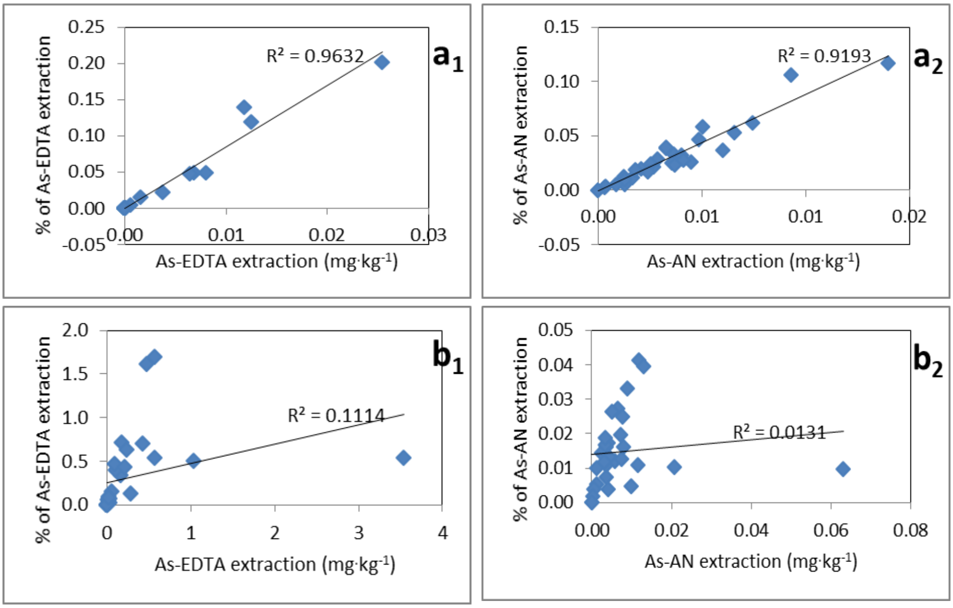
Such a high amount of arsenic in the soil in the area of Mitrovica is a consequence of the mining and processing activity that took place in this area in the past. Other authors have also reported high levels of arsenic in soils around mining areas, such as in the region of Freiberg, Germany, around 970 km^2 have been defined as contaminated with arsenic, where over 50% of the soil has shown a value above 55 mg kg^{-1} (Loukola-Ruskeeniemi *et al.*, 2022). Also near Verdun, France, studies have shown high levels of arsenic ranging from 15 mg kg^{-1} in the reference zone to 775 mg kg^{-1} in the highly contaminated site (Loukola-Ruskeeniemi *et al*., 2022).

In the area of Mitrovica according to the research of Stafilov *et al.* 2010, about 124 km^2 is above the target value according to the standard of Kosovo (30 mg kg^{-1}), while 64km^2 was above 55mg kg^{-1}, and which, according to the Kosovo standard, must be constantly monitored. As a result of the developed human activities in this area, As content at different levels has been reported from 2.1 to 3900 mg kg^{-1} (Aliu *et al*., 2019). Also, Barać *et al.* (2016) reported arsenic levels in floodplain agricultural soils along Iber River vary from 15 to 473 mg kg^{-1}. Student T-test has shown statistical significance in the pseudo-tatal content of arsenic in the researched areas ($p<0.01$) (table 1).

Bioavailability and mobile form of Arsenic in soil

The potential bioavailability form of arsenic in agricultural soils is given in graphic 1. As can be seen from the graph, the largest amount of As was extracted in the area of Mitrovica with 1.7% (graph 1 b), while in the area of Drenas this amount reached up to 0.2% (graph 1 a). The extracted mobile amount of As in agricultural soils showed higher values in the Drenas region with a maximum of 0.117 % (graph 1 a) compared to the Mitrovica region where this value only reached 0.041 % (graph 1 b). Similar results for the researched region have been reported by other authors, such as Barać *et al*. (2016); Nanoni *et al.* (2011).

Student T-test has shown statistical significance in the bioavailability and mobile form of arsenic in between the researched areas ($p<0.01$ and $p<0.05$ respectively) (table 1).



Graphic 1. The extracted amount of bioavailability of arsenic from the total in percentage and $mg \cdot kg^{-1}$ (a_1-potential bioavailability of As in Drenas region; a_2-mobile form of As in Drenas region; b_1-potential bioavailability of As in Mitrovica region; b_2-mobile form of As in Mitrovica region)

As shown in Table 2, the forms of arsenic showed a high correlation of 95% between As-AR and As-EDTA and As-EDTA with As-AN, respectively 91% between As-AR and As-AN. While their correlation with soil parameters has been weak.

Table 2. Correlation between forms of Arsenic and other properties

	pH CaCl2	*Clay %*	*N, %*	*C, %*	As-AR	*As-EDTA*	*As- AN*
pH CaCl2	1						
Clay %	0.40752985	1					
N, %	0.49249711	0.3982004	1				
C, %	0.46487709	0.4037168	0.975366	1			
As-AR	0.01374274	-0.219468	-0.059385	-0.118140	1		
As-EDTA	0.05698793	-0.225327	-0.052818	-0.102330	0.95262889	1	
As- AN	0.15932609	-0.167231	0.091207	0.036003	0.91727208	0.95580905	1

CONCLUSIONS

In the region of Drenas, all the analyzed samples were within the target values, while in the Mitrovica region, 50% of the analyzed samples were within the target values, 30% were within the accepted values but which require further research and 20% of the samples were above the allowed values for the content of arsenic in agricultural soils.

High concentration of arsenic has been noticed close to the sources of pollution, sometimes exceeding the allowed values several times. Since these lands are used for agricultural production, such a high amount of arsenic can be dangerous for human health and other organisms.

The potentially bioavailable and mobile form of arsenic has shown low extraction rates, however, due to the very high correlation of these forms with the total amount of arsenic, it can enter the food chain and may cause a health risk. The content of arsenic in the agricultural lands of the two regions has shown significant differences between them.

We recommend to the authorities responsible for land management to make a plan for soil remediation, especially in areas with high levels of arsenic. This can be achieved through phytoremediation using hyper accumulating plants such as sunflower, sorghum, lupine, etc. This can also be combined with bioremediation, namely the use of microbiological processes to convert arsenic into a less toxic form. We suggest also to farmers in these lands to produce plants that do not accumulate arsenic.

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