

## ECOLOGICAL RISK ASSESSMENT OF SOIL CONTAMINATION BY POTENTIALLY TOXIC ELEMENTS. CASE STUDY: MITROVICA REGION, REPUBLIC OF KOSOVO

Milihate Aliu,<sup>1\*</sup> Robert Šajn,<sup>2</sup> Trajče Stafilov<sup>3,4\*</sup>

<sup>1</sup>*Department of Industrial Engineering with Informatics, Faculty of Engineering and Informatics, University of Applied Sciences in Ferizaj, Str. Universiteti nn, 70000 Ferizaj, Republic of Kosovo*

<sup>2</sup>*Geological Survey of Slovenia, Dimičeva 14, 1000 Ljubljana, Slovenia*

<sup>3</sup>*Institute of Chemistry, Faculty of Natural Sciences and Mathematics*

*“Ss Cyril and Methodius” University in Skopje, POB 162, 1001 Skopje, North Macedonia*

<sup>4</sup>*Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts, Blvd. Krste Misirkov 2, 1000 Skopje, North Macedonia*

\*[milihate.aliu@ushaf.net](mailto:milihate.aliu@ushaf.net) // \*[trajcest@pmf.ukim.mk](mailto:trajcest@pmf.ukim.mk)

**A b s t r a c t:** This study aimed to investigate the input of various potentially toxic elements (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) into the surface soils of the Mitrovica region, a historically active Pb–Zn mining and metallurgical area in Kosovo. Geochemical analyses and multivariate statistics revealed a strong contamination pattern resulting from anthropogenic inputs of these elements. An ecological risk assessment of soil contamination by these potentially toxic elements was conducted in this region using various indicators. The contamination factors showed extremely high values for Au, Pb, Sb, Cd, As, and Ag compared to European and global background values, indicating very high to extreme soil contamination. The enrichment factors confirmed significant to extremely high enrichment for most elements except Mo and Tl. The geo-accumulation indexes indices categorized soil as moderately to extremely contaminated, especially for Pb, Ag, As, Bi, Cd, and Zn. The values of both indicators show highly to extremely contaminated soils with most of the analyzed elements, particularly in the cities of Zvečan and Mitrovica. The cumulative ecological risk index was more than thirty times higher than the critical threshold, indicating a serious threat to soil quality and ecological health.

**Key words:** soil; potentially toxic elements; pollution; ecological risk; Mitrovica region; Republic of Kosovo

### INTRODUCTION

Environmental pollution from anthropogenic activities has resulted in both direct and indirect contamination of all natural ecosystems. Potentially toxic elements (PTEs) are chemical elements that pose a significant environmental concern due to their toxicity, persistence, and bioaccumulation in humans, animals, and plants (Kabata-Pendias, 2011; Nieder et al., 2018; Li et al., 2018; Nieder and Benbi, 2023; Thalassinou et al., 2023). Although these elements occur naturally in soils at varying background concentrations, they often reach much higher levels in areas affected by anthropogenic activities such as mining, smelting, and various industrial processes. Mining and smelting operations frequently release high concentrations of Pb, Zn, Cd, Sb, As, and Hg into surrounding soils,

creating permanent pollution hotspots (Stafilov et al., 2010; Wu et al., 2018). In particular, areas where Pb and Zn are mined often show elevated concentrations of Pb, Zn, Cd, and Sb, elements known for their toxicity and environmental persistence (Lindberg & Malm, 2019). This accumulation often leads to soil contamination, which can pose significant ecological risks and adverse effects on human health (Khan et al., 2021).

Long-term exposure to PTEs has been associated with various adverse health effects, including carcinogenicity and damage to multiple organ systems such as the central and peripheral nervous systems, gastrointestinal tract, cardiovascular system, haematopoietic system, renal system, and circulatory system (Briffa et al., 2020; Badamasi et

al., 2024). Some of these PTEs are essential micronutrients at low concentrations, but at higher levels they pose serious risks, particularly in soils near industrial areas. These soils can contaminate crops grown there, threatening human health through food consumption (Alloway, 2013; Shen et al., 2019).

Mining, metallurgy, and other anthropogenic activities have polluted the city of Mitrovica and its surroundings, causing serious ecological and environmental problems. In a previous study, elements such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo were found in soil samples as an anthropogenic association resulting from the mining and processing of Pb-Zn ore in the Mitrovica region of the Republic of Kosovo (Šajn et al., 2013). Among the potentially toxic elements, Pb remains one of the best-studied, as humans have been exposed to lead on a large scale since ancient times. Lead is a non-biodegradable metal that occurs in nature in relatively small quantities. The concentration of lead in the atmosphere is constantly increasing due to human activities such as manufacturing, mining and the burning of fossil fuels. Children living near such sites are also at risk of elevated blood lead concentrations (Wani et al., 2015). Lead is highly persistent, bioaccumulative, and neurotoxic, and particularly impairs children's cognitive development. Most information on human lead exposure and its health effects is based on blood lead levels. Lead poisoning remains a serious problem among children in the towns of Zvečan and Mitrovica, due to high lead exposure (Factor-Litvak et al., 1990; Musliu et al., 2008; HRW, 2009; Boisa et al., 2013; Brewer et al., 2016; Shabani et al., 2019; Kastrati et al., 2024).

Cadmium, often associated with Zn and Pb ores, is highly mobile in acidic soils and can easily penetrate plant tissue, posing a risk of food chain contamination (Alloway, 2013). Cadmium is present as a pollutant in non-ferrous metal smelters and electronic waste recycling. Zinc, lead, and copper mines and smelters contribute to the release of this metal into the atmosphere, leading to soil contamination (Yang et al., 2025). Zinc is an essential element for most living organisms and plays a key role in enzyme processes, cell metabolism, immune function, protein synthesis, DNA synthesis, and cell division (Kiouri et al., 2023). Although Zn toxicity is relatively low, poisoning can occur in both acute and chronic forms (Johnson et al., 2007; Mitra et al., 2022).

Copper is also an essential micronutrient for humans and animals, as it is required to maintain the

strength and health of blood vessels, nerves, and bones (Scheiber et al., 2013). Although copper occurs naturally in soils, its accumulation is largely influenced by anthropogenic activities, particularly mining, smelting, industrial emissions, and intensive agricultural practices. Elevated copper levels in the blood can cause abdominal pain, vomiting, nausea, diarrhoea, and may damage kidney and liver function (ATSDR, 2022). In addition to geological sources and industrial pollution, other anthropogenic sources related to agricultural activities can also increase copper content in soils (Panagos et al., 2018).

Arsenic, often found in sulphide ore deposits, is a carcinogenic metalloid that contaminates soils (WHO, 2001; IARC, 2012). High exposure to arsenic through ingestion can cause problems in the digestive and nervous systems, as well as in cardiac activity (ATSDR, 2007). Environmental contamination by arsenic from anthropogenic and natural sources has occurred in many parts of the world and is now recognized as a global problem (Noble et al., 2010). The main anthropogenic sources of soil contamination with arsenic include base metal smelters and the mining of arsenic, lead, zinc, and gold (Drewniak et al., 2010). Once absorbed into the body, arsenic binds to haemoglobin, plasma proteins, and leukocytes, then spreads to various organs such as the liver, kidneys, lungs, spleen, and intestines. Chronic exposure to arsenic is associated with peripheral neuropathies and an increased risk of various malignancies, particularly of the skin, lungs, and liver (Hughes, 2002).

The chemistry and geochemistry of antimony are most similar to those of arsenic, which is usually associated with non-ferrous deposits. Its emissions to the atmosphere originate from non-ferrous metal mining and from the primary and secondary smelting of non-ferrous metals, especially lead, copper and zinc (Ettler et al., 2010). Antimony can accumulate in the human body through direct inhalation, ingestion, and absorption through skin contact (Gebel, 1997).

Mercury, a globally monitored toxic metal, remains a concern due to its persistence and neurotoxic effects (Lindberg & Malm, 2019). Most mercury contamination originates from coal smelting and combustion, and it is highly toxic and bioaccumulative (Bernhoft, 2012). Inhalation of high concentrations of mercury vapour can cause coughing, chills, fever, shortness of breath, and sometimes nausea, vomiting, and diarrhoea. Continuous exposure to elemental mercury can lead to accumulation

in the body and permanent damage to the nervous system and kidneys (Jackson, 2018). Elements such as Ag and Au are less toxic in bulk but serve as indicators of mining-related contamination. Silver is a rare, naturally occurring metal that often occurs as a mineral ore in combination with other elements. Silver in any form is not considered toxic to humans (ASTDR, 1990). The study area, Mitrovica town and surroundings, has long been known for mining and smelting, and gold was recovered from the electrolysis of the silver refinery in the Trepça complex (Dushi, 2009).

Although molybdenum is an important trace element for human health, it can be toxic at high doses (Mendel, 2013). Higher levels of molybdenum are found in the air near industries that process or release molybdenum, as well as near mining and milling operations (Cortada et al., 2018). The smelting of chalcogenic ores, particularly lead and zinc sulphides, produces thallium emissions that contribute to soil contamination (Gomez-Gonzalez et al., 2015). Thallium is highly

toxic even at low concentrations (John Peter & Viraraghavan, 2005).

Monitoring potentially toxic elements in the soil of the Mitrovica region and its surroundings is highly important. However, there is a lack of studies employing geochemical indices or assessing the potential ecological risk from anomalous concentrations of PTEs in the soils of Mitrovica and its surroundings. Therefore, it is necessary to continually investigate the concentrations of these elements and their accumulation in the soils to ensure that permissible levels are not exceeded. The objectives of this study were: (1) to determine the current concentrations of potentially toxic elements (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) in the soils of the Mitrovica region, Republic of Kosovo; (2) to assess the input and distribution of these elements using geochemical indices, including the geo-accumulation index ( $I_{geo}$ ) and the enrichment factor (EF); and (3) to assess the ecological risk of these potentially toxic elements using established risk assessment methods.

## MATERIAL AND METHODS

### Study area

The study area (Figure 1) is extensive, measuring 24 km NNW–SSE by 18 km WWS–EEN, and is defined by the coordinates (WGS 84) 20.74528°–20.99235° E and 42.78522°–42.99330° N. The Mitrovica region is an area affected with a significant mining industry, as the Trepça mines, a large mining and metallurgical complex, located in this region. The lead and zinc ore mines of Trepça are complex, containing Ag, Au, Bi, Sb, Cd, Cu, Mn, In, Ge, Te, Ta, Se, and S in addition to Pb and Zn. From 1930 to the present, the Trepça mine has produced 625,000 t of lead concentrates, 685,000 t of zinc concentrates, 444,000 t of pyrite concentrates, and a mixed concentrate of lead and copper in the flotation plants (Dushi, 2002).

The metallurgical process of lead extraction leaves behind slag with a Pb content of 1–12%. At the end of the process, a large amount of slag is deposited elsewhere. The metallurgical extraction of zinc leaves 16–20% of this metal in the form of sludge, which is deposited in a landfill in the industrial area. It is estimated that the sludge contains more than 50,000 t of Zn, Cd, and other metals. More than 15 million tonnes of rich waste from the processing of Pb and Zn are stored in the residues of the Trepça flotation in Zvečan. These landfills are

potentially significant sources of metals that can be transported by rivers and wind, resulting in the dispersion of large quantities of air pollutants over a wide area and their deposition in the soil. This industrial waste also contributes in pollution of surface water and sediments in the basin of Ibër and Sitnica rivers (Ferati et al., 2015; Kadriu et al., 2016, 2019).

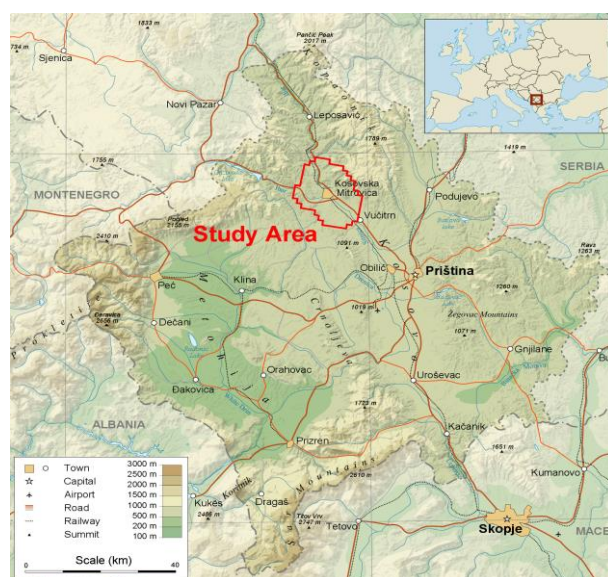
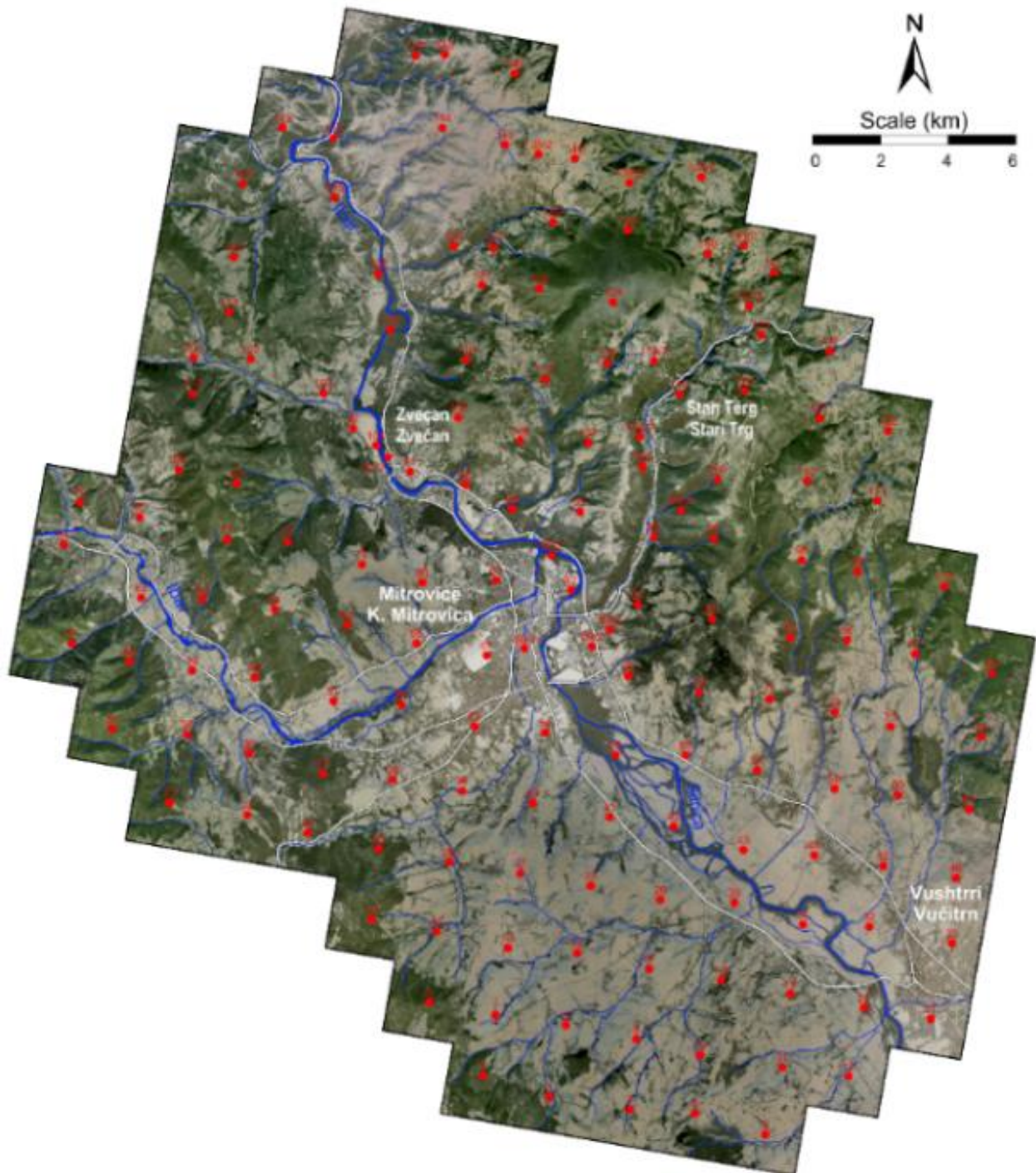


Fig. 1. Location of the investigated area

### *Sampling and sample preparation*

A total of 156 soil samples were collected from the 301.5 km<sup>2</sup> study area (Figure 2). The soil samples were taken from a depth of 0 – 0.5 cm. The sampling protocol was adapted according to European studies (Reimann & Caritat, 1998; Theocharopoulos et al., 2001) and experience in a similar region (Stafilov et al., 2010). After impurities were removed, the soil samples were air-dried, sieved

through a plastic sieve with a mesh size of 2 mm, and then ground to less than 0.125 mm fraction size in an agate mill. The soil powders were digested with aqua regia (a mixture of HNO<sub>3</sub>, HCl, and water at 95 °C) using the 1DX1 method (Šajn et al., 2013; Aliu et al., 2019). The digested solutions were analyzed for Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo using inductively coupled plasma mass spectrometry (ICP-MS).



**Fig. 2.** Map showing the soil collection points in the study area

### Contamination evaluation

The enrichment factor was calculated using the formula introduced by Buat-Menard & Chesselet (1979) and Adnan et al. (2022) as shown in Equation 1.

$$EF = \frac{(C_n/C_{ref})_{Sample}}{(B_n/B_{ref})_{EU/World}}, \quad (1)$$

where  $C_n$  is the content of the target element (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) in the soil sample, and  $C_{ref}$  is the content of the reference element (typically Mn, Al, Sr, Fe, or Ti) in the soil sample.  $B_n$  is the content of the analyzed chemical element in the soils of the study area, and  $B_{ref}$  is the content of the reference element in the soils of Europe or the world. In this study, aluminium was used as the reference element in EU and world soils, with average values of 58,000 mg/kg (Salminen et al., 2005) and 155,000 mg/kg (Rudnick & Gao, 2004), respectively. The aluminium content in the soil of the entire study area was 12,000 mg/kg (Šajin et al., 2013). The enrichment factor (EF) was calculated as the average value of the ratio between the average content of each soil sample from the entire study area and the average values of the analyzed elements in the top soils of the EU (Salminen et al., 2005) and in the soils of the world (Rudnick and Gao, 2004). Generally, enrichment factor values below 2 indicate no or minimal enrichment; values between 2 and 5 indicate moderate enrichment; values between 5 and 20 indicate significant enrichment; values between 20 and 40 indicate very high enrichment; and EF values above 40 indicate extremely high enrichment (Adnan et al., 2022).

The degree of contamination with potentially toxic elements in the soil of the study area was assessed using the geo-accumulation index ( $I_{geo}$ ), calculated according to the method proposed by Müller (1979), as shown in Equation 2:

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 * B_n} \right), \quad (2)$$

where  $C_n$  is the measured content of the analyzed metal in each soil sample, and  $B_n$  is the geochemical background value of the same metal. The value of 1.5 is a constant factor used to account for possible variations in the background data due to lithological differences and to detect very small anthropogenic influences. The  $I_{geo}$  value was calculated using the two average values for the Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo content in Europe (Salminen et al., 2005) and worldwide (Rudnick and Gao, 2004). Müller (1981) defined seven classes for

the geo-accumulation index, ranging from class 0 to class 6. The  $I_{geo}$  classifies the degree of soil contamination as follows: uncontaminated ( $I_{geo} \leq 0$ ), uncontaminated to moderately contaminated ( $0 < I_{geo} \leq 1$ ), moderately contaminated ( $1 < I_{geo} \leq 2$ ), moderately to heavily contaminated ( $2 < I_{geo} \leq 3$ ), heavily contaminated ( $3 < I_{geo} \leq 4$ ), strongly to extremely contaminated ( $4 < I_{geo} \leq 5$ ), and extremely contaminated ( $I_{geo} > 5$ ). The highest class (class 6) reflects an enrichment factor at least 100 times higher than the background value.

The contamination factor (CF) was calculated to assess the degree of contamination in the soils of the study area with potentially toxic elements (PTEs), following the methodology introduced by Håkanson (1980). The CF quantifies the extent of contamination by comparing the measured concentration of each element in the soil with the corresponding background concentration, which represents natural levels unaffected by anthropogenic inputs. The calculation is based on Equation 3:

$$CF = \frac{C_i}{B_i}, \quad (3)$$

where  $C_i$  is the concentration of the analyzed chemical element (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) in the soil samples and  $B_i$  is the geochemical background concentration of the respective element in the soils of the EU (Salminen et al., 2005) and the soils of the world (Rudnick and Gao, 2004). According to Håkanson's (1980) classification, CF values are interpreted as follows:  $CF < 1$  indicates low contamination;  $1 \leq CF < 3$ , moderate contamination;  $3 \leq CF < 6$ , considerable contamination; and  $CF \geq 6$ , very high contamination.

In general, soil contamination is not caused by a single potentially toxic element, but by a combination of several elements. It is therefore important to assess the overall contamination of the soil with heavy metals. The metal pollution index (MPI) quantifies the cumulative pollution from different elements that contribute to an increased risk of metal toxicity (Li et al., 2018). A metal pollution index greater than 1 ( $MPI > 1$ ) indicates polymetallic soil pollution, while  $MPI < 1$  indicates no polymetallic pollution. According to Jahan and Strezov (2018), six pollution classes are defined based on increasing metal pollution levels:  $MPI < 1$  – unpolluted;  $1 < MPI < 2$  – slightly polluted;  $2 < MPI < 3$  – moderately polluted;  $3 < MPI < 5$  – moderately to heavily polluted;  $5 < MPI < 10$  – severely polluted; and  $MPI > 10$  – heavily polluted. The metal pollution index (MPI) was calculated as the geometric

mean of the individual CF values based on the formula originally proposed by Tomlinson et al. (1980), as presented in Equation 4.

$$\text{MPI} = \sqrt[n]{\text{CF}_1 \cdot \text{CF}_2 \cdot \text{CF}_3 \cdot \dots \cdot \text{CF}_i}, \quad (4)$$

where,  $\text{CF}_i$  is the contamination factor for each analyzed potentially toxic element (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) in the soil samples from the study area, and  $n$  is the total number of analyzed elements.

### Ecological risk assessment

The ecological risk factor ( $E_r$ ), given by Håkanson (1980), is a quantitative measure that expresses the potential ecological risk of a specific pollutant based on the toxicity of heavy metals and the sensitivity of the surrounding environment. The ecological risk factor ( $E_r^i$ ) for a single heavy metal was calculated according to the method proposed by Håkanson (1980) using Equation 5.

$$E_r^i = T_r^i \cdot \text{CF}^i, \quad (5)$$

where  $T_r^i$  is the toxic response factor for element  $i$ , and  $\text{CF}^i$  is the contamination factor for the same element  $i$ . The calculated  $E_r^i$  values are interpreted according to the following risk classification:  $E_r^i < 40$  indicates low risk;  $40 \leq E_r^i < 80$ , moderate risk;  $80 \leq E_r^i < 160$ , considerable risk;  $160 \leq E_r^i < 320$ , high risk; and  $E_r^i \geq 320$ , extremely high risk. These numerical categories reflect the varying degrees of potential ecological threat posed by individual heavy metals in the soil.

The standardized toxic response factors ( $T_r^i$ ) used in this study were as follows: As = 10, Cd = 30, Cu = 5, Hg = 40, Pb = 5, and Zn = 1, based on the generally accepted classification of Håkanson (1980). For Ag and Sb, values of 17.5 and 7, respectively, were taken from Aksu et al. (1998) and Li et al. (2018), corresponding to current applications in environmental risk assessments. The elements Bi, Au, Tl, and Mo were excluded from the calculations of the ecological risk factor ( $E_r$ ) as there are no standardized toxic response factors for them. To maintain methodological consistency and reliability of the ecological risk factor ( $E_r$ ), only elements with well-established  $T_r^i$  values were included in the risk assessment.

Consequently, the potential ecological risk index (RI) was calculated exclusively for Ag, As, Cd, Cu, Hg, Pb, Sb, and Zn, for which reliable and standardized toxic response factors ( $T_r^i$ ) are available. This selective approach ensures methodological consistency and increases the accuracy and reliability of the ecological risk assessment.

Accordingly, the RI value is determined as the sum of the individual ecological risk factors ( $E_r^i$ ) of these potentially toxic elements in soils, as shown in Equation 6.

$$\text{RI} = \sum E_r^i, \quad (6)$$

where RI is the total potential ecological risk index for all assessed heavy metals (Ag, As, Cd, Cu, Hg, Pb, Sb, and Zn) and  $E_r^i$  is the individual ecological risk factor for a given element  $i$ . The risk index can be classified as low risk ( $\text{RI} < 150$ ), moderate risk ( $150 \leq \text{RI} < 300$ ), considerable risk ( $300 \leq \text{RI} < 600$ ), and very high risk ( $\text{RI} \geq 600$ ) (Ahamad et al., 2020).

## RESULTS AND DISCUSSION

### Distribution of potentially toxic elements in soils

A previous study found that elements such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo (Šajn et al., 2013; Aliu et al., 2019) occurred in soil samples as an anthropogenic association resulting from mining and processing of Pb-Zn ore in the Mitrovica region, Republic of Kosovo (Šajn et al., 2013). The lack of comprehensive studies and consistent environmental assessment does not mean there are no risks to the environment or public health. Therefore, an ecological risk assessment of soil contamination by these PTEs was carried out in

this region using various indicators. The concentrations of the analyzed elements were determined in 156 surface soil samples (0–5 cm depth). The descriptive statistics for the element concentrations are shown in Table 1, while their spatial distribution maps are presented in Figure 3.

The median concentrations of the individual elements across the entire sampling area were as follows: Pb > Zn > Cu > As > Au > Sb > Cd > Bi > Mo > Ag > Tl > Hg. The results show that among these elements, Pb, Zn, As, and Cu, are the dominant elements in the soils of the studied region, followed by Cd, Bi, Mo, Ag, Tl, and Hg (Table 1).

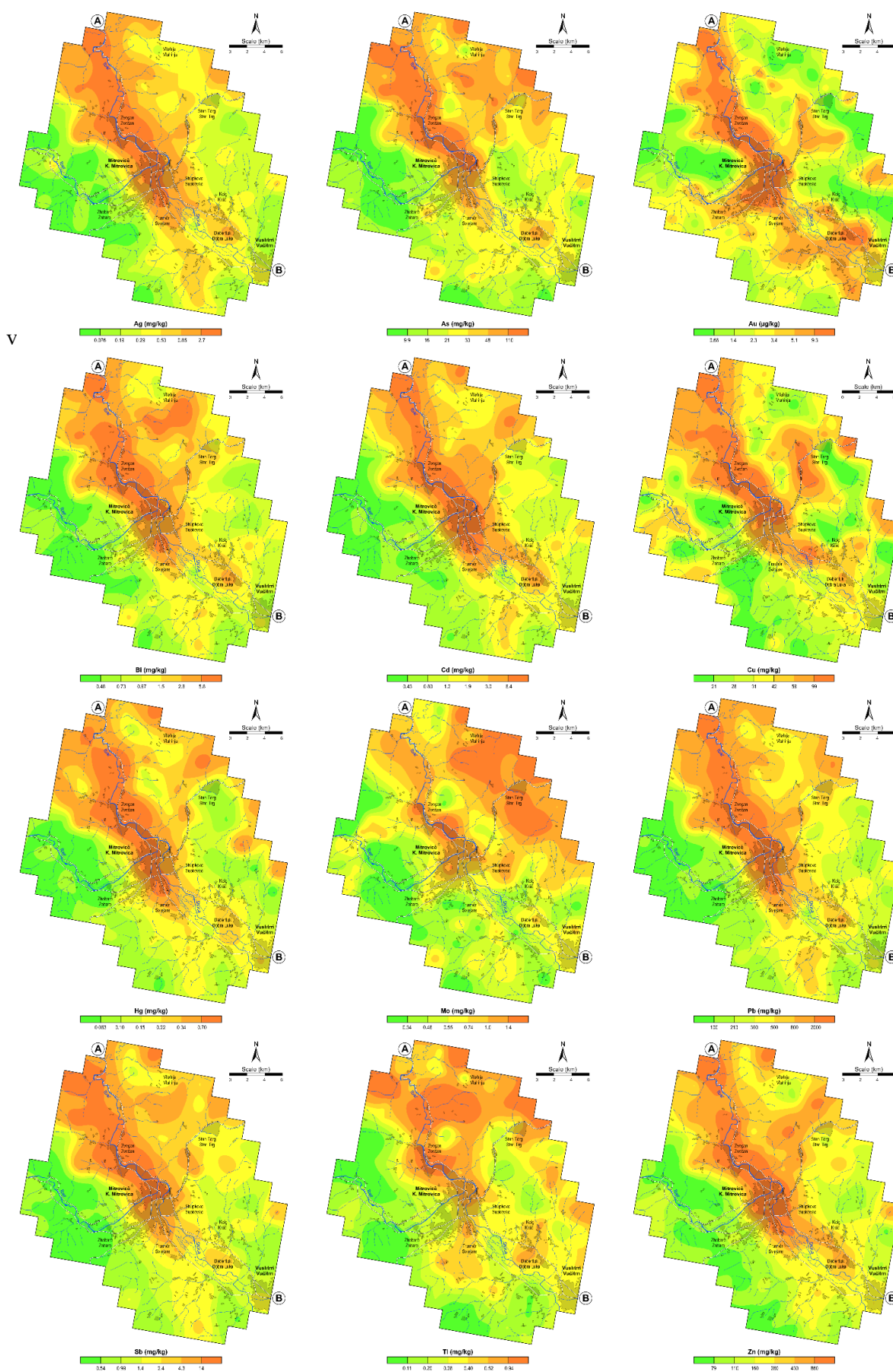


Fig. 3. Spatial distribution maps of the studied elements

Table 1

Basic statistical data on the contents of the studied elements in the soil (in mg/kg)

Element	X	S	Md	P <sub>10</sub>	P <sub>90</sub>	Min	Max	Dutch standards	
								Target	Action
Ag	0.44	4.2	0.40	0.050	3.2	0.050	58	–	15
As	30	3.1	25	9.2	150	2.1	3900	29	30
Au	2.7	3.8	2.8	0.25	12	0.25	170	–	–
Bi	1.5	3.3	1.1	0.50	7.2	0.10	110	–	–
Cd	1.6	3.0	1.4	0.40	10	0.10	47	0.8	12
Cu	42	2.3	35	17	120	9.0	1600	36	190
Hg	0.20	3.0	0.15	0.060	0.74	0.020	11	0.3	10
Mo	0.68	2.0	0.70	0.30	1.5	0.050	5.7	3.0	200
Pb	450	3.4	370	110	2300	34	35000	85	530
Sb	2.3	4.2	1.7	0.60	16	0.10	1400	3.0	15
Tl	0.33	2.6	0.30	0.10	1.2	0.050	7.7	1.0	15
Zn	240	3.0	170	76	1200	32	12000	140	720

X – arithmetical mean, S – arithmetical standard deviation, Md – median, P<sub>10</sub> – 10 percentiles, P<sub>90</sub> – 90 percentiles, Min – minimum, Max – maximum.

Of this group of PTEs, only Au and Bi are not included in the Dutch pollutant standards (VROM, 2000). The target values of the new Dutch list are exceeded in soil across almost the entire study area (301.5 km<sup>2</sup>), while the action values apply to about 122 km<sup>2</sup>. The anthropogenic contamination is a consequence of historical Pb-Zn mining, processing, and smelting, which resulted in high concentrations of As, Cd, Cu, Hg, Pb, and Zn in the topsoil. The contaminated area includes the urban areas of Mitrovica and Zvečan, as well as the Trepça mine complex (Šajn et al., 2013).

The spatial distribution maps of the analyzed elements in the study area are presented in Figure 3. The highest values are observed in the urban areas of Mitrovica and Zvečan, the Trepça mine complex, and the alluvial plains of the Ibër river. Contamination extends to the slopes of the Kopaonik mountains in the north of the study area and to the Rogozna mountains in the north-northeast. The highest levels are recorded at sampling points in the town of Zvečan and its surroundings, as well as in the town of Mitrovica. The lowest levels are found in the urban area of Vushtrri (Šajn et al., 2013).

#### Soil contamination evaluation

Several geochemical indices, including the enrichment factor (EF) (Covelli & Fontolan, 1997)

and the geo-accumulation index ( $I_{geo}$ ) (Müller 1981), are commonly used to distinguish between geogenic and anthropogenic sources of soil element contamination (Shaheen et al., 2019). These indices are based on the total concentrations of elements in the samples, which can be influenced by pedo-geochemical processes such as weathering, soil formation, and regional geological differences. The enrichment factor (EF) assesses the degree of metal enrichment in soils (Kowalska et al., 2016). The geo-accumulation index ( $I_{geo}$ ) assesses the degree of metal contamination in soils (Li et al., 2018) and identifies which metals are enriched in the soil (Shruti et al., 2018).

In this study, EF and  $I_{geo}$  were used to assess the contamination levels of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo in the soils of the study area and the cities of Zvečan, Mitrovica and Vushtrri. Both indicators were calculated following the methodologies proposed by Covelli & Fontolan (1997) and Müller (1979), based on the average concentrations of these elements in the study area and the three cities, using the average background concentrations of these elements in European soils (Salminen et al., 2005) and global soils (Rudnick & Gao, 2004) (Table 2).

Table 2

Average contents of PTEs in the study area, in the towns of Zveçan, Mitrovica, and Vushtrri, European soils, and in the continental crust (world soils), given in mg/kg

Element	No of samples					
	Europe <sup>a</sup>	World <sup>b</sup>	Study area	Zveçan	Mitrovica	Vushtrri
Ag	0.304	0.053	0.44	5	11	8
As	7.0	4.8	30	570	55	22
Au*	0.001	0.0015	0.0069	0.0061	0.0086	0.005
Bi*	0.18	0.16	1.5	51	4.5	0.89
Cd	0.15	0.09	1.6	20	7.0	1.3
Cu	13	28	42	510	80	34
Hg	0.061	0.05	0.20	3.9	0.54	0.18
Mo	0.943	1.1	0.68	1.8	0.92	0.56
Pb	23	17	450	16000	1700	250
Sb	1.04	0.40	2.3	190	7.9	1.1
Tl	0.821	0.9	0.33	1.6	0.45	0.26
Zn	52	67	240	3500	940	180

<sup>a</sup>Salminen et al., 2005; <sup>b</sup>Rudnick & Gao, 2004

The enrichment factor values show that soils in the Mitrovica region are enriched with the analyzed potentially toxic elements in the following order: Pb > Cd > Bi > As > Ag > Sb > Hg > Zn > Cu > Au > Mo > Tl (Table 3).

In the soils of the region, lead and cadmium are the most highly enriched toxic elements, followed by bismuth, arsenic, silver, antimony, mercury, zinc, copper, and gold, while molybdenum and thallium are the least enriched. The EF data for Pb (EF > 40) indicate extreme enrichment of surface soils throughout the study area (Table 3). Cadmium, Bi, As, and Ag also show very high enrichment, with EF values above 20. The EF values for Sb ranges from 16 to 42, indicating significant to very high enrichment. Surface soils in the study area are also significantly enriched in Hg, Zn, Cu, and Au. These high EF values confirm the influence of anthropogenic sources, indicating that the soils are primarily polluted by human activities. The EF data for Mo and Tl show the lowest values among the analyzed elements, ranging from 0.79 to 0.92 and from 0.67 to 0.73, respectively, indicating that the surface soils are not, or are only slightly, enriched with these elements (Table 3).

Table 3

Enrichment factors of analyzed elements in the soils of the study area

Background values	Study area	Major cities		
		Zveçan	Mitrovica	Vushtrri
Ag				
European soils <sup>a</sup>	17.9	123	8.9	1.1
World soils <sup>b</sup>	133	707	51	6.3
As				
European soils	17.6	105	10.2	4.07
World soils	29.3	153	14.8	5.92
Au				
European soils	6.93	79.8	11.1	6.45
World soils	4.62	52.5	7.40	4.30
Bi				
European soils	25.1	366	32.3	6.39
World soils	28.2	412	36.3	7.18
Cd				
European soils	28.0	172	60.3	11.2
World soils	31.3	287v	100	18.7
Cu				
European soils	7.56	50.7	7.95	3.38
World soils	3.51	23.5	3.69	1.57
Hg				
European soils	18.1	82.6	11.4	3.81
World soils	22.1	101	14.0	4.65
Mo				
European soils	0.92	2.46	1.26	0.77
World soils	0.79	2.11	1.08	0.66
Pb				
European soils	57.3	899	95.4	14.0
World soils	77.5	1216	129	19.0
Sb				
European soils	16.4	236	9.81	1.37
World soils	42.8	613	25.5	3.55
Tl				
European soils	0.73	2.51	0.71	0.41
World soils	0.67	2.30	0.65	0.37
Zn				
European soils	13.0	86.9	23.3	4.473
World soils	10.1	67.4	18.12	3.47

<sup>a</sup>Salminen et al. 2005; <sup>b</sup>Rudnick & Gao, 2004.

EF < 2 – no or minimal enrichment, 2 < EF < 5 – moderate enrichment, 5 < EF < 20 – significant enrichment, 20 < EF < 40 – very high enrichment, EF > 40 – extremely high enrichment.

For urban soils, the enrichment factors indicate that the urban soils of Vushtrri (a non-industrial area) are not enriched with Mo and Tl ( $EF < 1$ ); are minimally enriched in Ag ( $EF = 1-2$ ); moderately enriched in Cu, Hg, Sb, and Zn ( $EF = 2-5$ ); and significantly enriched in As, Au, Bi, Cd, and Pb ( $EF = 5-20$ ). In contrast, the surface soils of Zvečan show moderate enrichment for Mo and Tl ( $EF = 2-5$ ), and extremely high enrichment for Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, and Au ( $EF > 40$ ), indicating high to extremely high contamination by these potentially toxic elements (Table 3). In Mitrovica EF values show greater variability: extremely high enrichment ( $EF > 40$ ) for Cd and Pb; high enrichment ( $EF = 20-40$ ) for Bi and Zn; significant enrichment ( $EF = 5-20$ ) for Ag, As, Au, Cu, Hg, and Sb; while Mo and Tl show no or minimal enrichment ( $EF < 1$ ) (Table 3).

The degree of contamination of surface soils in the Mitrovica region, as indicated by the geo-accumulation index ( $I_{geo}$ ), shows that almost all sampling points exceed the critical threshold of  $I_{geo} > 0$  (Table 4).

According to the classification by Müller (1969), soils in the study area are heavily contaminated with Pb ( $3 < I_{geo} \leq 4$ ); moderately to heavily contaminated with Bi and Cd ( $2 < I_{geo} \leq 3$ ); moderately contaminated with As, Sb, Hg, and Zn ( $1 < I_{geo} \leq 2$ ); uncontaminated to moderately contaminated with Au ( $0 < I_{geo} \leq 1$ ); and uncontaminated with Mo and Tl ( $I_{geo} \leq 0$ ) (Table 4). Surface soils in the city of Zvečan have the highest  $I_{geo}$  values for Ag, Pb, Sb, Bi, Zn, Cd, As, and Hg ( $I_{geo} > 5$ ) and are extremely contaminated with these elements (Table 4). Surface soils in the city of Mitrovica are also extremely contaminated with Cd and Pb ( $I_{geo} > 5$ ), highly to extremely contaminated with Ag, Bi, and Sb ( $4 < I_{geo} \leq 5$ ), highly contaminated with Hg and Zn ( $3 < I_{geo} \leq 4$ ), and moderately to highly contaminated with Cu ( $2 < I_{geo} \leq 3$ ). In contrast, surface soils in Vushtrri are moderately polluted with Hg and Sb ( $1 < I_{geo} \leq 2$ ), moderately to heavily polluted with As and Au ( $2 < I_{geo} \leq 3$ ), heavily polluted with Cd and Pb ( $3 < I_{geo} \leq 4$ ), and practically unpolluted with Mo and Tl ( $I_{geo} \leq 0$ ) (Table 4).

The contamination factor (CF) reflects the anthropogenic contribution to elemental pollution and is often used as a measure of total soil pollution (Dantu, 2009). The calculated minimum and maximum CF values for the analyzed elements (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo) in the soils of the study area, based on the respective element concentrations in EU (Salminen et al., 2005) and world (Rudnick & Gao, 2004) soils, are presented in Table 5.

Table 4

*Geo-accumulation index of analyzed elements in the soils of the study area using European background values and continental crust (world soils)*

Background value	Study area	Major cities		
		Zvečan	Mitrovica	Vushtrri
Ag				
European soils <sup>a</sup>	2.18	6.57	2.79	-0.22
World soils <sup>b</sup>	4.60	9.01	5.23	4.64
As				
European soils	1.52	6.35	2.97	3.14
World soils	2.06	6.89	3.52	2.20
Au				
European soils	0.49	2.60	3.10	2.32
World soils	-0.09	4.07	2.52	3.33
Bi				
European soils	2.48	8.15	4.64	2.30
World soils	2.65	8.31	4.81	5.56
Cd				
European soils	2.89	7.06	5.54	3.11
World soils	3.62	7.80	6.28	3.85
Cu				
European soils	1.08	5.29	2.62	1.39
World soils	0.03	4.19	1.51	0.28
Hg				
European soils	1.20	6.00	3.15	1.56
World soils	1.48	6.28	3.43	1.85
Mo				
European soils	-1.03	0.93	-0.03	-0.75
World soils	-1.25	0.71	-0.26	-0.97
Pb				
European soils	3.69	9.44	6.21	3.44
World soils	4.12	9.88	6.64	3.88
Sb				
European soils	0.59	7.51	2.92	1.06
World soils	1.96	8.89	4.30	1.46
Tl				
European soils	-1.84	0.96	-0.68	-1.86
World soils	-1.97	0.83	-1.00	-1.79
Zn				
European soils	1.63	5.49	3.59	1.21
World soils	1.26	5.70	3.81	1.42

<sup>a</sup>Salminen et al., 2005; <sup>b</sup>Rudnick & Gao, 2004.

$I_{geo} \leq 0$  – uncontaminated,  $0 < I_{geo} \leq 1$  – uncontaminated to moderately contaminated,  $1 < I_{geo} \leq 2$  – moderately contaminated,  $2 < I_{geo} \leq 3$  – moderately to heavily contaminated,  $3 < I_{geo} \leq 4$  – heavily contaminated,  $4 < I_{geo} \leq 5$ , heavily to extremely contaminated,  $I_{geo} > 5$  – extremely contaminated.

Table 5

Minimum, maximum and average values of CF according to the European and global average contents

Element	European background			World background		
	Min	Max	Average	Min	Max	Average
Ag	0.10	556	23	0.47	3188	132
As	0.30	569	16	0.44	829	23
Au	0.02	169	6.9	0.02	113	4.6
Bi	0.56	675	25	0.62	759	28
Cd	0.67	76	312	1.1	520	36
Cu	0.68	122	5.8	0.31	57	2.7
Hg	0.33	16.4	18	0.40	2000	22
Mo	0.05	6.0	0.92	0.05	5.2	0.79
Pb	1.5	434	44	2.0	588	60
Sb	0.10	1448	16	0.25	3766	43
Tl	0.06	9.4	0.73	0.06	8.6	0.67
Zn	0.61	192	10	0.48	149	7.8

CF < 1 – low contamination, 1 ≤ CF < 3 – moderate contamination, 3 ≤ CF < 6 – considerable contamination, CF ≥ 6 – very high contamination.

The order of the average CF values based on the EU background values is Cd > Pb > Bi > Ag > Hg > Sb > As > Zn > Au > Cu. The values for Mo and Tl are below 1, although for some samples in the study area the CF is relatively high (with a maximum value of 6.0 for Mo and 9.4 for Tl). Very similar results are obtained when the CF is calculated using the global background values. According to the classification of Håkanson (1980), almost all analyzed soils from the study area (except for Co, Mo, and Tl) appear to be highly contaminated (Table 5). Very high CF values were also recorded for soils in the major cities of the region, especially in the areas of Zvečan and Mitrovica (Table 6).

The metallic pollution index (MPI) was calculated using the contamination factors (CF) of the analyzed elements, with background values for European and global soils. The MPI values for the study area and the towns of Zvečan, Mitrovica, and Vushtrri are shown in Table 7.

These results indicate that combined pollution from all analyzed elements leads to heavily polluted soils throughout the entire study area and in Zvečan, heavily polluted soils in Mitrovica, and moderately polluted soils in Vushtrri. The results in Table 7 also reveal only minor differences between the MPI values calculated using EU background concentrations

(Salminen et al., 2005) and global background concentrations (Rudnick and Gao, 2004), indicating significantly elevated levels of all analyzed elements in both the entire study area and the main towns of the region (Zvečan, Mitrovica, and Vushtrri).

Table 6

Average values of CF according to the European and global average contents for the soils of the major cities in the region

Element	Zvečan		Mitrovica		Vushtrri	
	EU	World	EU	World	EU	World
Ag	95.4	547	6.91	39.6	0.86	4.91
As	81.4	119	7.86	11.5	3.14	4.58
Au	6.10	4.07	8.60	5.73	5.00	3.33
Bi	283	319	25.0	28.1	4.94	5.56
Cd	133	222	46.67	77.8	8.67	14.4
Cu	39.2	18.2	6.15	2.86	2.62	1.21
Hg	63.9	78.0	8.85	10.8	2.95	3.60
Mo	1.91	1.64	0.98	0.84	0.59	0.51
Pb	696	941	73.9	100	10.87	14.7
Sb	183	475	7.60	19.7	1.06	2.75
Tl	1.95	1.78	0.55	0.50	0.32	0.29
Zn	67.3	52.2	18.1	14.0	3.46	2.69

Table 7

Metallic pollution index (MPI) values for potentially toxic elements in the study area and main urban centres using background values for European and the world soils

Background value	Study area	Zvečan	Mitrovica	Vushtrri
European soils	12.1	47.8	8.6	2.4
World soils	12.0	59.1	10.6	2.9

MPI < 1 – unpolluted; 1 < MPI < 2 – slightly polluted; 2 < MPI < 3 – moderately polluted; 3 < MPI < 5 – moderately to heavily polluted; 5 < MPI < 10 – severely polluted; MPI > 10 – heavily polluted.

The calculated values of ecological risk factors ( $E_r^i$ ) across the study area show considerable variability among these elements (Table 8), reflecting their differing toxicities and contamination levels. This variability highlights the complex nature of soil contamination in the region and underscores the

need to assess each element individually in terms of its ecological risk.

Table 8

*Values of the toxic response factors ( $T_r^i$ ), the ecological risk factors ( $E_r^i$ ), and the potential ecological risk index (RI) for potentially toxic elements in the soils of the study area*

Element	Ag	As	Cd	Cu	Hg	Pb	Sb	Zn
$T_r^i$	17.5	10	30	5	40	5	7	1
$E_r^i$	1670	2787	4709	309	3613	3808	3366	116
RI	20377							

Cadmium has the highest ecological risk factor of 4709 (Table 8), indicating an extremely high potential ecological threat due to its high toxicity and mobility in the environment. Mercury follows with an  $E_r^i$  value of 3613 (Table 8), emphasising its known toxicity and persistence, which pose serious environmental and health risks. Lead also presents a very high-risk level, with an ecological risk factor of 3808, related to its widespread use and release through mining and industrial activities. Antimony has a similarly high-risk factor of 3366, indicating considerable contamination and toxic potential in the analyzed soils. The  $E_r^i$  value for arsenic is 2787, confirming a significant ecological risk, which is alarming given the carcinogenic properties of arsenic. Silver and copper show moderate to high risk values with  $E_r^i$  values of 1670 and 309, respectively, reflecting their occurrence in high concentrations,

but comparatively lower toxicity factors. Finally, zinc has the lowest risk factor among the elements considered at 116, indicating a relatively low ecological threat due to its essential role in biological systems and comparatively low toxicity.

According to the classification by Håkanson (1980), the ecological risk assessment of soils in the study area shows that Cd, Hg, Pb, Sb, As, and Ag fall into the extremely high-risk category ( $E_r^i \geq 320$ ), indicating a serious potential threat to the environment. Copper is classified as a high ecological risk ( $160 \leq E_r^i < 320$ ), while Zn poses a considerable risk ( $80 \leq E_r^i < 160$ ) (Table 8). The dominance of Cd, Hg, Pb, Sb, As, and Ag in the higher risk categories emphasises their critical contribution to the overall ecological burden and highlights the urgent need for targeted environmental monitoring and management strategies.

Based on the calculated values of the ecological risk factor ( $E_r^i$ ) for the eight potentially toxic elements (Cd, Hg, Pb, Sb, As, Ag, Cu, and Zn), the cumulative potential ecological risk index (RI) for the study area was determined to be 20,377 (Table 8). According to the classification proposed by Håkanson (1980), an RI value greater than 600 indicates an extremely high ecological risk. This exceptionally high RI value reflects a significant cumulative impact of several toxic elements and strongly indicates severe anthropogenic contamination, probably due to historical mining, metallurgical, and industrial activities in the region. The high ecological risk emphasises the urgent need to monitor the environment, further investigate the mobility and bioavailability of contaminants, and consider targeted mitigation strategies to reduce the long-term risks to ecological systems and human health.

## CONCLUSION

In this study, soil contamination by potentially toxic elements (PTEs) such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl, and Mo was analyzed in detail in the Mitrovica region, a historic industrial area in Kosovo. The results indicate widespread pollution, mainly caused by former mining and metal processing activities. Elements such as Pb, Cd, As, and Ag were found at extremely high concentrations, well above environmental safety limits. Maps of the spatial distribution of the analyzed elements show that the highest levels occur in the urban areas of Mitrovica and Zvečan, the Trepça mine complex, and the alluvial plains of the Ibër river, confirming

the anthropogenic impact of mining and metal processing in this region.

An ecological risk assessment of soil contamination by these PTEs was conducted out using various indicators. The contamination factors (CF) showed extremely high values for Au, Pb, Sb, Cd, As, and Ag compared to EU background values, indicating very high to extreme soil contamination. The enrichment factors (EF) confirmed significant to extremely high enrichment for most elements except Mo and Tl. The geo-accumulation indices categorized the soils as moderately to extremely contaminated, especially for Pb, Ag, As, Bi, Cd, and Zn.

Both indicators point to highly to extremely contaminated soils with most of the analyzed elements, particularly in the cities of Zvečan and Mitrovica. The cumulative ecological risk index (RI) of 20,377 was more than thirty times higher than the critical threshold ( $RI \geq 600$ ), indicating a serious threat to soil quality and ecological risk. In addition, metal pollution index (MPI) values above 10 confirm severe polymetallic contamination throughout the

study area. Although large-scale remediation measures are not currently required, continuous measures monitoring and targeted, site-specific assessments are recommended to manage potential environmental and health risks. Future studies should also consider evaluating the potential impacts of PTEs on human health through comprehensive risk assessments.

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## Резиме

### ЕКОЛОШКА ПРОЦЕНА НА РИЗИК ОД КОНТАМИНАЦИЈА НА ПОЧВАТА СО ПОТЕНЦИЈАЛНО ТОКСИЧНИ ЕЛЕМЕНТИ. ТЕМАТСКА СТУДИЈА: РЕГИОН НА МИТРОВИЦА, РЕПУБЛИКА КОСОВО

Милихате Алиу<sup>1\*</sup>, Роберт Шајн,<sup>2</sup> Трајче Стафилов,<sup>3,3\*</sup>

<sup>1</sup>Оддел за иновативно инженерство со информатика, Факултет за инженерство и информатика, Универзитет за применети науки во Феризај, ул. „Универзитет“ бб, 70000 Феризај, Република Косово

<sup>2</sup>Геолошки завод на Словенија, Димичева 14, 1000 Љубљана, Словенија

<sup>3</sup>Институт за хемија, Природно-математички факултет, Универзитет Св. Кирил и Методиј во Скопје, Архимедова 5, 1000 Скопје, Северна Македонија

<sup>4</sup>Испирајувачки центар за животна средина и материјали, Македонска академија на науките и уметностите, Бул. Крсте Мисирков 2, 1000 Скопје, Северна Македонија

\*milihate.aliu@ushaf.net // \*trajcest@pmf.ukim.mk

**Клучни зборови:** почва; потенцијално токсични елементи; индекси на загадување; еколошки ризик; регион на Митровица; Република Косово

Целта на оваа студија беше да се испита внесувањето потенцијално токсични елементи (PTEs) Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl и Mo во површинските почви на регионот на градот Митровица, историски активна рударска

и металуршка област во Косово. Геохемиските анализи и мултиваријантната статистика утврдија силен модел на контаминација што произлегува од присуство на овие елементи во почвата како резултат на антропогени влијанија.

Процената на еколошкиот ризик од контаминација на почвата од овие елементи во овој регион е спроведена со користење различни индикатори. Факторите на контаминација покажаа екстремно високи вредности на Au, Pb, Sb, Cd, As и Ag во споредба со нивната содржина во почвите во Европа, како и глобалните позадински вредности, што укажува на многу висока до екстремна контаминација на почвата. Факторите на збогатување потврдија значајно до екстремно високо загадување со повеќето елементи (освен

Mo и Tl). Индексите на геоакмулација ги категоризираа почвите како умерено до екстремно контаминирани, особено за Pb, Ag, As, Bi, Cd и Zn. Вредностите на двата индикатора покажуваат високо до екстремно контаминирани почви со повеќето анализирани елементи, особено за почвите од градовите Звечан и Митровица. Кумулативниот индекс на еколошки ризик е повеќе од триесет пати повисок од критичниот праг, што укажува на сериозна закана за квалитетот на почвата и еколошкото здравје.