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# Assessment of soil contamination by cadmium, chromium, vanadium, and antimony near a mining tailings dump in Graçanica, Kosovo

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## ABSTRACT

Heavy metal contamination near mining sites poses serious and long-term risks to environmental integrity and public health. This study investigates the concentrations, spatial distribution, and geochemical behavior of cadmium (Cd), chromium (Cr), vanadium (V), and antimony (Sb) in soils surrounding the Graçanica tailings dump in Kosovo, a site historically affected by decades of Pb-Zn ore processing. Soil samples were collected from residential and adjacent areas using standardized protocols and analyzed via inductively coupled plasma–optical emission spectrometry (ICP-OES) at the Horn & Co. Analytics SH.P.K. Laboratory in Pristina. Measured concentrations ranged from 4.5–8.6 mg/kg for Cd, 139–783 mg/kg for Cr, 45–89 mg/kg for V, and 4.3–31 mg/kg for Sb, all exceeding permissible limits set by Kosovo, the EU, and WHO/FAO soil quality standards. Spatial analysis revealed peak concentrations near the tailings dump and the Graçanica River, with a declining gradient away from the source—indicating localized pollution from mining activities. Soil pH ranged from 3.95 to 7.73, suggesting that acidic conditions enhance metal mobility and bioavailability. Correlation and pH analysis showed that Cd and Sb exhibit high mobility under acidic conditions, while Cr and V display redox-sensitive behavior, reflecting complex geochemical interactions and multiple contamination sources. These findings highlight the need for targeted remediation, sustained environmental monitoring, and comprehensive health risk assessments. This study also highlights the persistent legacy of mining pollution in Kosovo and contributes critical data for sustainable land management and policymaking.

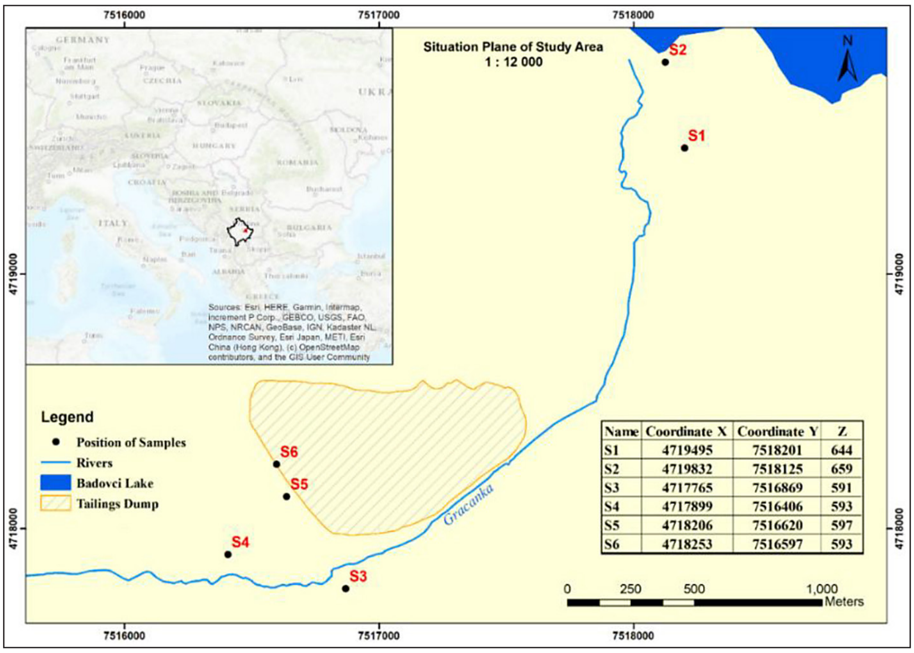
**Keywords:** heavy metals, mining tailings, soil contamination, bioaccumulation, ICP-OES.

## INTRODUCTION

Mining is a key economic sector in the Republic of Kosovo, which is rich in polymetallic deposits—particularly of lead (Pb) and zinc (Zn)—often associated with valuable metals such as silver (Ag), gold (Au), chromium (Cr), nickel (Ni), iron (Fe), cobalt (Co), aluminum (Al), copper (Cu), and manganese (Mn). Additionally, Kosovo possesses a wide range of rare and strategic elements, including antimony (Sb), niobium (Nb), lanthanum (La), cerium (Ce), scandium (Sc), zirconium (Zr), molybdenum (Mo), tungsten (W), indium (In), and rhenium (Re) [1,2]. This exceptional geological endowment positions the mining sector as a driver of national development, with significant potential for industrial growth and strategic integration into global mineral markets.

However, the economic benefits of mining come at an environmental cost. The extraction and processing of ore generate substantial waste, including gangue and flotation residues. In Kosovo, decades of Pb-Zn ore processing—particularly through flotation—have led to the uncontrolled accumulation of mining waste, which poses serious threats to soil, water, and air quality [3–5]. Poorly managed tailings dumps are a legacy of past mining practices and represent long-term sources of pollution.

One critical site is the Graçanica tailings dump, located near the Kizhnica ore deposit, part of the Hajvali–Badovc–Kizhnica ore field in the

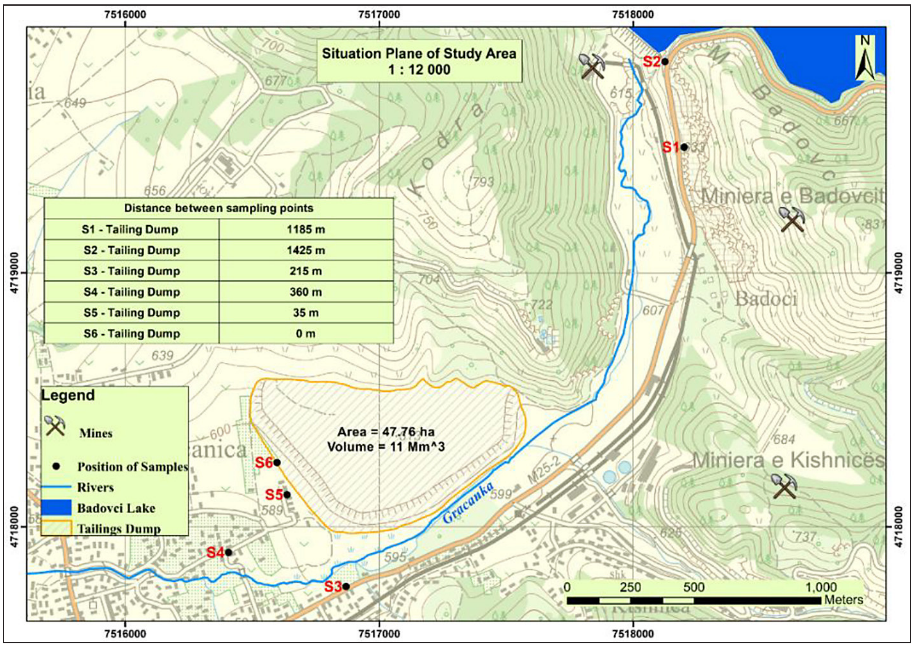


| Name | Coordinate X | Coordinate Y | Z |
|---|---|---|---|
| S1 | 4719495 | 7518201 | 644 |
| S2 | 4719832 | 7518125 | 659 |
| S3 | 4717765 | 7516869 | 591 |
| S4 | 4717899 | 7516406 | 593 |
| S5 | 4718206 | 7516620 | 597 |
| S6 | 4718253 | 7516597 | 593 |

**Figure 1.** Geographical location of the tailings dump in Graçanica Municipality, Kosovo, including GPS-referenced positions of the soil sampling sites

southern Trepça Mineral Belt—Kosovo's most historically significant mining region [6] (Figure 1). The Graçanica dump spans approximately 47.76 hectares and holds an estimated 11 million tons of flotation residues from Pb-Zn ore processing at the Kizhnica Flotation Plant. Residential areas lie just 30–150 meters from the site, raising serious concerns over the potential dispersal of toxic elements into surrounding ecosystems and communities (Figure 2).

Mining activities contribute to a wide range of environmental impacts, including soil erosion, water contamination, loss of biodiversity, and air pollution (Figure 3). Among the most hazardous by-products are heavy metals such as cadmium (Cd), Cr, vanadium (V), and antimony (Sb),



| Distance between sampling points | |
|---|---|
| S1 - Tailing Dump | 1185 m |
| S2 - Tailing Dump | 1425 m |
| S3 - Tailing Dump | 215 m |
| S4 - Tailing Dump | 360 m |
| S5 - Tailing Dump | 35 m |
| S6 - Tailing Dump | 0 m |

**Figure 2.** Location of the 47.76 ha legacy tailings dump in Graçanica, Kosovo, containing approximately 11 million Mt of Pb-Zn processing residues. The figure also shows the sampling locations and their respective distances from the tailings dump

which are known for their persistence, toxicity, and bioaccumulative potential [7–9]. While some metals occur naturally in trace amounts, elevated concentrations are largely the result of anthropogenic activities—especially mining and industrial emissions. Over time, these elements accumulate in soil, air, water, and biota, posing long-term risks to human and ecosystem health (Figure 4).

The persistence of heavy metals in the environment is particularly concerning. For example, the half-life of Cd in soil can reach 280 years, while Pb can remain for up to 2,000 years [3, 5, 10, 11]. Their environmental behavior—mobility, solubility, and bioavailability—is influenced by various factors, including pH, redox potential, mineralogy, and hydrogeological conditions [5, 12]. Unlike geogenic sources, which release metals slowly through natural weathering, anthropogenic inputs rapidly disturb geochemical balances, leading to uneven distribution and higher contamination levels.

In mining areas dominated by sulfide mineralization—such as the Hajvali–Badovc–Kizhnica zone—oxidation of sulfide-bearing tailings can accelerate metal mobilization and increase the risk of contamination in nearby soils and waterways [13–16]. These transformations enhance the mobility and ecological impact of toxic metals, especially in areas lacking proper containment or remediation.

Soil pH plays a central role in controlling heavy metal dynamics. Metal solubility and speciation are highly pH-dependent, which affects their mobility, bioavailability, and toxicity. In acidic soils, for instance, metals become more soluble and more likely to migrate into groundwater or be taken up by plants—thus entering the food chain [17, 18]. This study investigates the accumulation and distribution of four potentially toxic elements—Cd, Cr, V, and Sb—in soils near the Graçanica tailings dump. Special attention is given to pH-dependent metal mobility and the proximity of residential areas to contaminated zones. The research aims to assess environmental and public health risks associated with long-term exposure to these heavy metals. Findings will contribute to the broader understanding of contamination pathways in post-mining landscapes and support the development of effective environmental management, land-use planning, and remediation strategies.

Adopting a multidisciplinary approach that integrates environmental geochemistry, soil science, and public health perspectives is essential. Such research is critical not only for assessing ecological risk but also for informing evidence-based policies aimed at safeguarding natural resources and promoting sustainable development in mining-affected regions.

## MATERIALS AND METHODS

### Sampling strategy and study design

This study was conducted as part of the project "Heavy Metals Pollution and the Ecological Risk Assessment of the Graçanica Tailings Dump", funded by the Ministry of Education, Science, Technology and Innovation of the Republic of Kosovo and the Austrian Development Agency. The sampling strategy aimed to assess

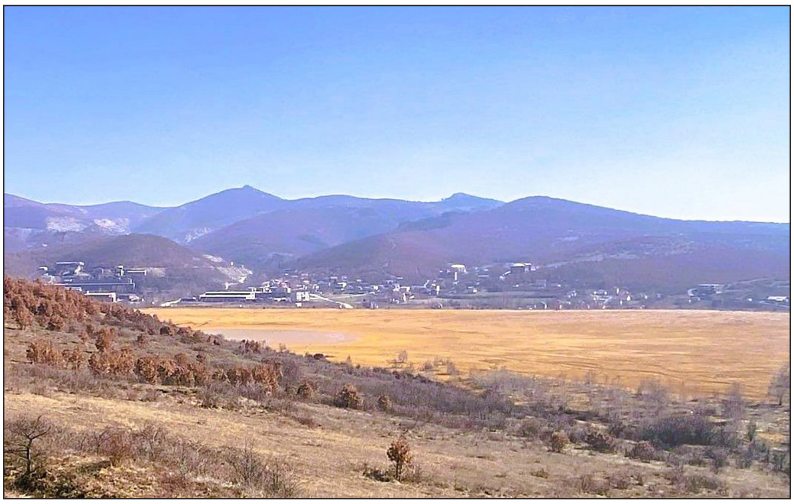


**Figure 3.** Legacy tailings dump lacking effective containment or remediation measures, increasing the long-term risk of toxic metal leaching into surrounding environmental compartments (Photo: March 2025)

**Figure 4.** The immediate vicinity of the tailings dump to inhabited areas presents a critical risk to local ecosystems and human health due to long-term exposure pathways (Photo: January 2025)

the environmental impact and spatial distribution of heavy metal contamination surrounding the Graçanica mining tailings dump.

Soil samples were collected systematically at varying distances and orientations from the tailings site to evaluate potential contamination gradients. Two samples (S1 and S2) were taken 1.185 m and 1.425 m to the north-northeast of the dump, respectively. Three samples (S3, S4, and S5) were collected from arable soils within residential zones to the south and southwest, at distances of 215 m, 360 m, and 35 m. One sample (S6) was collected directly at the edge of the tailings dump (0 m) on its southwestern boundary (Figure 2). Each sample was obtained using a standardized soil auger to a depth of 30 cm, yielding approximately 3 kg of material. Sampling procedures adhered to ISO/IEC 17025:2017 standards [19], ensuring methodological consistency and data reliability. Locations were georeferenced using GPS instrumentation (Figure 1). To avoid cross-contamination, samples were sealed and transported to a certified laboratory (Horn & Co. Analytics SH.P.K., Pristina) under controlled conditions for chemical analysis.

### Chemical analysis

Soil samples were analyzed for Cd, Cr, V, and Sb concentrations using inductively coupled plasma optical emission spectrometry (ICP-OES), following the DIN EN ISO 11885:2009-09 standard [20]. Soil pH was determined in accordance with DIN EN ISO 10523:2012 [21]. All analytical procedures were performed by trained and certified personnel, with instrument calibration and quality control conducted per manufacturer specifications at Horn & Co. Analytics SH.P.K.

### Data analysis

Statistical evaluation was carried out to quantify heavy metal concentrations and pH values across sampling locations. Descriptive statistics and graphical representations were used to analyze spatial trends and inter-element variability. Pearson correlation coefficients were calculated to assess potential relationships among Cd, Cr, V, Sb, and pH. To evaluate environmental risk, measured concentrations were compared against permissible limits established by: The Administrative Instruction of the Government of the Republic of Kosovo [22], Relevant European Union directives [23, 24], World Health Organization (WHO) guidelines [25], and joint WHO/FAO standards [26].

## RESULTS AND DISCUSSIONS

The results of this study provide clear evidence of significantly elevated concentrations of toxic heavy metals—specifically Cd, Cr, V, and Sb—in the municipality of Graçanica, Kosovo. These elevated levels are closely linked to the long-term environmental impact of the “Hajvalia–Badovc–Kizhnica” mining complex and, in particular, the adjacent tailings dump resulting from decades of Pb-Zn ore processing at the Kizhnica flotation facility. In the absence of adequate environmental management and containment measures, prolonged exposure of the tailings to atmospheric precipitation and wind over more than sixty years has likely contributed to the widespread and persistent dispersal of these toxic elements. The resulting environmental degradation extends beyond the immediate vicinity of the tailings site into nearby residential and agricultural areas, posing significant risks to both ecological systems and public health.

### Cadmium

Cadmium (Cd) is a relatively rare but highly toxic heavy metal, commonly occurring as an impurity in zinc, lead, and copper ores. It often substitutes for zinc in minerals such as sphalerite (ZnS) and smithsonite ($ZnCO_3$), where it can constitute up to 0.5% by mass [27–29]. Primary cadmium minerals—such as greenockite (CdS), monteponite (CdO), and otavite ($CdCO_3$)—are rare and typically form secondarily through the weathering of Cd-bearing zinc ores [28].

The primary anthropogenic sources of cadmium in the environment include non-ferrous metal mining and smelting, phosphate fertilizers, fossil fuel combustion, and waste incineration [27]. Once released, cadmium is readily transported through the atmosphere, deposited onto soils and water bodies, and absorbed by plants—particularly in acidic soils, which increase its mobility and bioavailability [30].

Cadmium has no known biological function and is highly toxic to living organisms. It accumulates in plants, aquatic species, and human tissues—especially in the kidneys, liver, and bones—where it can cause severe and often irreversible damage [31, 32]. Due to its long environmental persistence and high mobility, cadmium poses a serious and sustained risk to ecosystems and public health [32]. In humans, cadmium has a biological half-life of 16–30 years, contributing to cumulative toxicity. Chronic exposure has been linked to a range of health effects, including kidney dysfunction, skeletal damage, elevated blood pressure, and respiratory disorders such as emphysema, bronchitis, and asthma [33].

Cd emerged as the most prominent contaminant in the Graçanica region. Measured concentrations ranged from 4.5 to 8.6 mg/kg (Figure 5), substantially exceeding international and national thresholds—0.8 mg/kg (WHO) [25], 3 mg/kg (Kosovo) [22], and 1–3 mg/kg (EU) [23]. Even at distant sites (S1: 6.0 mg/kg; S2: 4.9 mg/kg), levels surpassed permissible limits, indicating widespread dispersion (Figure 5).

The highest concentrations were observed in residential and agricultural areas (S3–S5), with S5 reaching 8.6 mg/kg—over 10 times the WHO guideline—raising concerns about cadmium uptake in crops and associated health risks (Figure 5). Compared to typical mining-impacted soils (1.5–3.0 mg/kg) [34], these values suggest severe enrichment due to prolonged mining activity.

Notably, S6, located adjacent to the tailings dump, showed a lower concentration (4.5 mg/kg), possibly reflecting historical dispersion patterns. The mean Cd level across all sites was 5.65 mg/kg, with a coefficient of variation (CV) of 0.26, (Table 1), suggesting moderate variability and overall diffuse contamination.

Soil pH emerged as a key factor influencing Cd mobility across the study area. At sites S1–S4, neutral to slightly alkaline conditions (pH 7.14–7.73), (Figure 6), likely reduced Cd solubility and limited its mobility. In contrast, the strongly acidic pH at site S5 (pH 3.95) corresponded with the highest Cd concentration (8.6 mg/kg), underscoring the role of low pH in enhancing Cd desorption

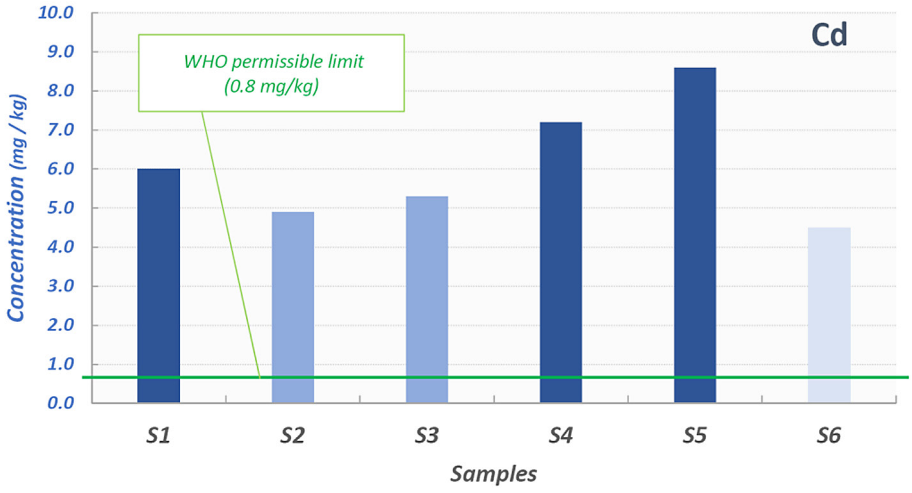


**Figure 5.** Cadmium concentrations in soil samples

**Table 1.** Statistical data on pH levels and heavy metal concentrations in soil samples

| Parameter | pH Value | Cadmium (Cd) | Chromium (Cr) | Vanadium (V) | Antimony (Sb) |
|---|---|---|---|---|---|
| Minimum [mg/kg] | 3.95 | 4.50 | 139.00 | 45.00 | 4.30 |
| Maximum [mg/kg] | 7.73 | 8.60 | 783.00 | 89.00 | 31.00 |
| Average [mg/kg] | 6.78 | 6.08 | 364.83 | 65.83 | 14.22 |
| Median [mg/kg] | 7.39 | 5.65 | 228.50 | 66.50 | 12.50 |
| Standard Deviation [mg/kg] | 1.45 | 1.56 | 285.21 | 16.07 | 9.30 |
| Coefficient of variation [-] | 0.21 | 0.26 | 0.78 | 0.24 | 0.65 |

and bioavailability (Figure 6). This relationship is further supported by a moderate negative correlation between pH and Cd levels (r = –0.61), indicating that acidic conditions significantly increase cadmium mobility and environmental risk.

Given cadmium's long biological half-life (10–30 years) [35] and its bioaccumulation in vital organs such as the kidneys, liver, and bones—causing irreversible damage and being linked to hypertension and respiratory illnesses [15, 31, 32]—its elevated presence in residential and agricultural soils represents a serious and persistent public health concern.

## Chromium

Chromium is moderately abundant in the Earth's crust (~100 µg/g), and its environmental and biological toxicity is highly dependent on its oxidation state [36]. Trivalent chromium (Cr III) is generally considered non-toxic and largely immobile in soils due to strong adsorption to soil particles. In contrast, hexavalent chromium (Cr VI) is highly toxic, mobile under oxidizing and alkaline conditions, and classified as a known human carcinogen. Cr (VI) is estimated to be 100–1.000 times more toxic than Cr (III), capable of bioaccumulating in vital organs such as the kidneys, liver, and brain, where it can induce genotoxic and carcinogenic effects [30].

Although Cr (III) is sometimes regarded as an essential trace element, its biological role remains uncertain. Elevated soil chromium levels, particularly in the hexavalent form, can inhibit plant growth and photosynthesis. Chromium primarily occurs as chromite ($FeCr_2O_4$) and, less commonly, as crocoite ($PbCrO_4$), typically concentrated in ultramafic rocks and mining regions. Major anthropogenic sources include steel production, metal processing, chemical manufacturing, and mining activities [30, 37].

According to WHO/FAO guidelines [26], the maximum permissible Cr concentration in soil is 100 mg/kg, while Kosovo's national limit is 300 mg/kg [22]. No specific threshold is defined under EU directives. All six sampling sites in the Graçanica area exceeded the WHO/FAO limit, with Cr concentrations ranging from 139 to 783 mg/kg—indicating substantial contamination (Figure 7). The highest levels were recorded at sites S2 (783 mg/kg) and S1 (670 mg/kg), both

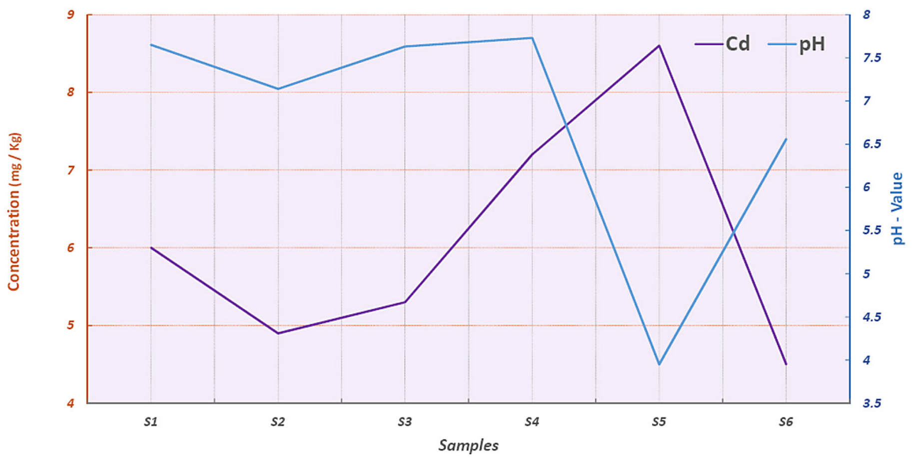


**Figure 6.** Variation in cadmium content as a function of pH in soil samples

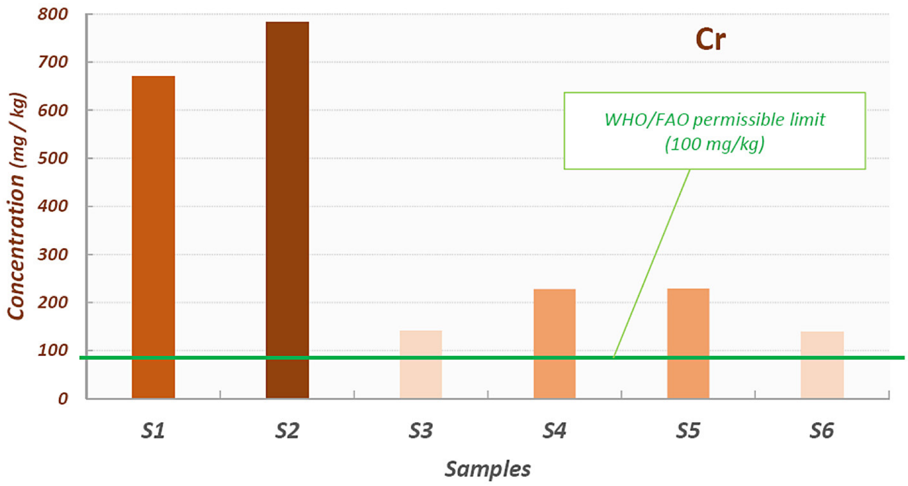


**Figure 7.** Chromium concentrations in soil samples

located near the “Hajvali–Badovc–Kizhnica” mining complex, suggesting a strong anthropogenic source. Notably, Cr at S2 was nearly eight times the WHO/FAO guideline (Figure 7). In comparison, lower concentrations were found at sites S3–S5 (140–229 mg/kg), while the lowest value was observed at S6 (139 mg/kg), located at the edge of the tailings dump (Figure 7).

The mean Cr concentration of 228.5 mg/kg exceeds WHO/FAO safety limits, with high spatial variability (CV = 0.78), (Table 1), likely driven by mining activity and local geochemical conditions. In areas with Pb-Zn sulfide deposits, identifying the mineralogical form and oxidation state of Cr is essential. Under oxidizing conditions, chromite ($FeCr_2O_4$) can release soluble chromate ions ($CrO_4^{2-}$) [28], which may react with $Pb^{2+}$ from galena to form crocoite ($PbCrO_4$)—a highly toxic mineral due to its combined chromium and lead content. Since this study measured only total chromium concentration, the results should be considered as a pilot assessment. They highlight the need for further research to distinguish between Cr (III) and the more hazardous Cr (VI) species.

The correlation coefficient between Cr content and soil pH was 0.26, indicating a weak positive relationship (Figure 8). This suggests a slight increase in Cr concentrations with rising pH, although the effect remains minimal—likely influenced by the relatively small samples size. According to [28], chromium speciation is strongly pH-dependent: trivalent chromium [Cr(III)] is stable under acidic to neutral conditions, whereas hexavalent chromium [Cr(VI)]—a more toxic and mobile form—is favored in alkaline soils. These findings confirm that total chromium contamination across the study area is both widespread and pronounced, particularly near industrial and mining activities. The consistently elevated Cr levels detected in all sampled sites raise significant

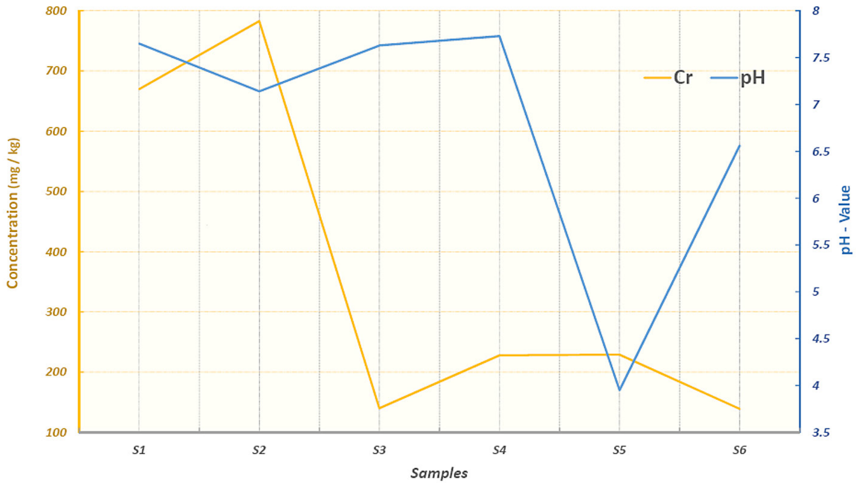


**Figure 8.** *V*ariation in chromium content as a function of pH in soil samples

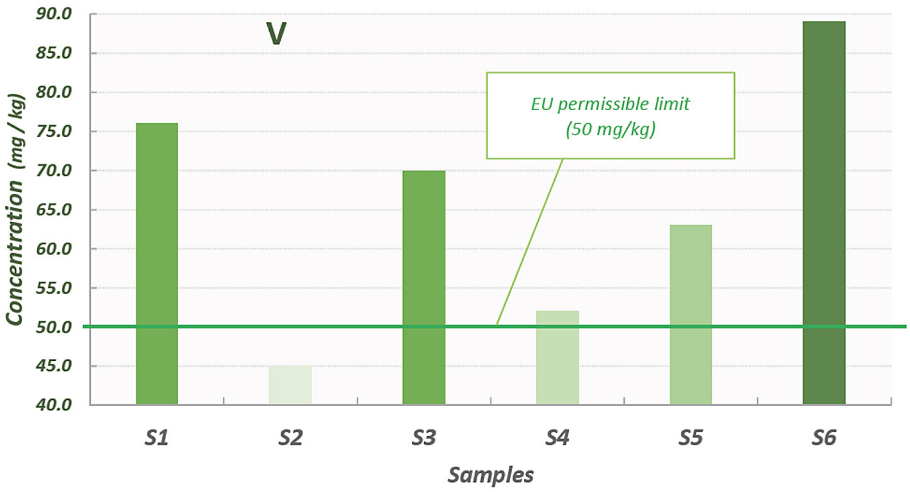


**Figure 9.** Vanadium concentrations in soil samples

concerns regarding soil quality degradation, phytotoxicity, and potential human exposure through the food chain.

## Vanadium

Vanadium (V) ranks 22nd in Earth's crust abundance, averaging ~150 mg/kg and distributed unevenly across rocks, soils, groundwater, fossil fuels, and organisms [38, 39]. Concentrations vary by lithology, from ~149 mg/kg in magmatic rocks to 0.0019 mg/kg in seawater [28]. Its complex chemistry arises from multiple oxidation states (+2 to +5), with +5 being most stable. Vanadium commonly occurs as V (III) in rocks, V (IV) in soils, and pentavalent vanadates complexed with metals like Cu, Zn, Pb, and Fe [30, 38].

Anthropogenic emissions, mainly from coal and crude oil combustion, surpass natural sources, with additional input from metal processing and mining [30,39].Vanadium compounds mimic phosphate, influencing chlorophyll synthesis and nitrogen fixation [40], but are also toxic and potentially carcinogenic [41]. Human exposure—through ingestion, inhalation, or occupational contact—can cause respiratory, renal, neurological issues, and chronic exposure may lead to "vanadism," characterized by mucosal inflammation and bronchial conditions [30, 40].

Vanadium concentrations in soil from six sampling sites in the Graçanica area ranged from 45 to 89 mg/kg, (Figure 9), with a median of 66.5 mg/kg and a coefficient of variation of 0.24 (Table 1), indicating moderate spatial variability. The highest level (89 mg/kg) was recorded at site S6, near the tailings dump, while the lowest (45 mg/kg) was at site S2, close to the Hajvali–Badovc–Kizhnicë ore field (Figure 9).

The EU recommends a vanadium threshold of 50 mg/kg in soil. All sites except S2 exceeded this limit, suggesting widespread contamination likely linked to mining and tailings activities. The Kizhnica region has a long history of lead and zinc mining. Vanadinite ($Pb_5(VO_4)Cl$), a secondary lead mineral, is commonly found in oxidized lead ore zones and may contribute to elevated vanadium levels. Further research is needed, to determine the forms and distribution of vanadium in soils near the mine and tailings dump.

Residential-agricultural sites (S3, S4, S5) showed elevated vanadium levels (52–70 mg/kg), likely due to leaching or atmospheric deposition from the nearby dump. Site S5 is particularly concerning due to its strongly acidic soil (pH 3.95) (Figure 10), which can increase vanadium mobility and groundwater contamination risk. While vanadium is typically more mobile in neutral to alkaline soils, soluble forms can also leach under acidic conditions. Vanadium is absorbed by plant roots and tends to accumulate in plant tissues. Though small amounts may promote growth, excessive levels can damage photosynthesis, development, and even cause cellular and genetic damage [39, 42].

The Pearson correlation coefficient between vanadium concentration and soil pH was weakly negative (r = –0.05), indicating an insignificant linear relationship (Figure 10). This suggests that vanadium mobility in the studied area is only minimally influenced by pH. Vanadium exists in multiple oxidation states ($V^{3+}$, $V^{4+}$, $V^{5+}$), and its solubility is governed not only by pH but also by redox conditions, soil composition, and organic matter content. Typically, $V^{3+}$ and $V^{4+}$ are relatively immobile under neutral and reducing conditions, whereas $V^{5+}$ becomes more soluble in acidic and oxidizing environments [28, 38].

The weak correlation may also result from external factors beyond soil pH, such as proximity to the tailings dump and Pb-Zn mining operations in Kizhnica, which can disrupt the natural relationship between vanadium concentration and pH—especially considering the limited sample size (n = 6). Overall, the results indicate localized total vanadium enrichment in the Graçanica area, primarily driven by mining activities. Elevated concentrations found both near the tailings dump and in residential-agricultural zones raise concerns regarding potential exposure risks via soil–water–plant pathways and airborne dust.

## Antimony

Antimony (Sb) is classified as a Critical Raw Material by the European Union due to its economic importance and limited availability in Europe [43]. It is used in flame retardants, lead-acid batteries, metal alloys, electronics, pigments, ceramics, rubber, ammunition, and defense applications. Despite its industrial relevance, Sb has a negligible recycling rate and is primarily recovered from lead-acid batteries [44, 45].

Geochemically less abundant than As, Sb typically occurs at low concentrations in groundwater [28]. It exists in three oxidation states (0, +3, +5), with Sb(III) being more mobile and toxic, especially under acidic conditions [44]. In soils, average Sb levels are approximately 1 ppm, while its crustal abundance ranges from 0.3 to 0.5 ppm. It commonly occurs as stibnite ($Sb_2S_3$) or senarmontite ($Sb_4O_6$) [44]. In the Janjevo deposit (Kizhnica–Hajvalia–Badovc ore field), pyrite contains up to 3.73% Sb, along with other toxic elements, raising concerns about acid mine drainage and metal mobilization [6, 43].

Sb's environmental behavior is complex and influenced by redox conditions, oxidation states, and interactions with Fe/Mn oxides and clay minerals [44, 46, 47]. Both natural and anthropogenic Sb contamination pose global risks. Sb toxicity—similar to arsenic—can affect the cardiovascular, respiratory, gastrointestinal, and nervous systems, and is considered carcinogenic [47]. However, key aspects of its environmental fate, mobility, and exposure pathways remain poorly understood.

Figure 11 clearly shows elevated Sb concentrations in samples S1, S2, S4, and S5, which recorded 13 mg/kg, 17 mg/kg, 12 mg/kg, and 31 mg/kg, respectively. These samples were collected from soils both distant from the tailings dump and from cultivated soils in residential areas to the south and southwest of the dump. Currently, Kosovo's Administrative Instruction does not specify permissible limits for Sb in soils, nor does the World Health Organization (WHO) provide such guidelines. However, according to European Union directives [24], the acceptable limit for Sb in soil is 10 mg/kg.

Samples S1 and S2, taken near the "Hajvalia–Badovc–Kizhnica" mining area, exceed the EU limit, likely due to historical mining emissions. In contrast, samples S3 (8 mg/kg) and S6 (4.3 mg/kg), collected from residential and agricultural zones adjacent to the tailings dump, remain below this threshold, indicating limited

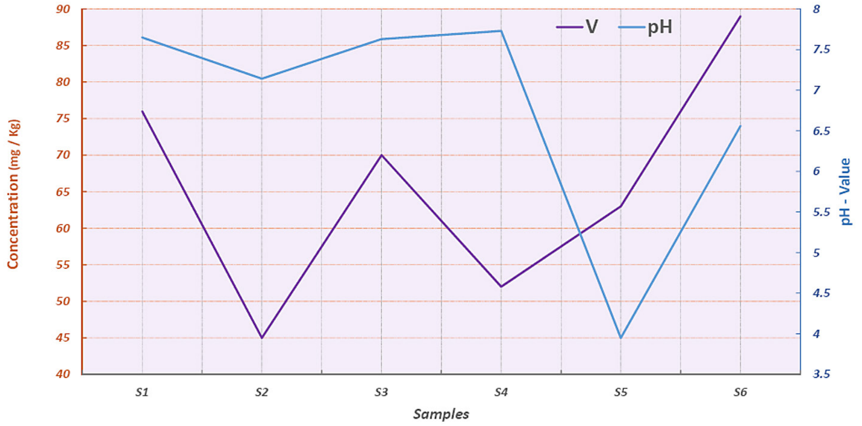


**Figure 10.** Variation in vanadium content as a function of pH in soil samples

contamination spread (Figure 11). Notably, sample S5 exhibited the highest Sb concentration (31 mg/kg), suggesting a potential contamination hotspot related to proximity to the tailings or localized accumulation.

Soil pH ranged from 3.95 to 7.73, encompassing both acidic and neutral conditions. A strong negative correlation (r = –0.78) between Sb concentrations and pH (Figure 12) suggests increased Sb mobility and bioaccumulation in acidic soils [44, 46]. Sample S5, with the lowest pH (3.95) (Figure 11), also showed the highest Sb concentration (31 mg/kg), reinforcing the link between soil acidity and Sb mobility.

These findings highlight the combined influence of mining legacy and soil acidification on Sb accumulation in contaminated soils. Accordingly, risk assessments in acidic soils near mining areas are critical—especially in agricultural zones where Sb uptake by crops could threaten food safety. This situation poses serious risks to both environmental and human health [48].

Soil pH is a critical factor influencing metal speciation, solubility, and bioavailability, often interacting with redox conditions and mineralogical composition. Although mineralogical composition and redox potential were not evaluated in this study, metal correlation diagrams suggest that Cd and Sb exhibit increased mobility under acidic conditions. This behavior is likely due to desorption from mineral surfaces and diminished adsorption onto clay minerals and organic matter. Furthermore, low pH enhances the solubility of Cd and Sb, thereby increasing their bioavailability. The mobility and toxicity of Cr and V are primarily governed by their oxidation states, which play a pivotal role in determining their environmental behavior.

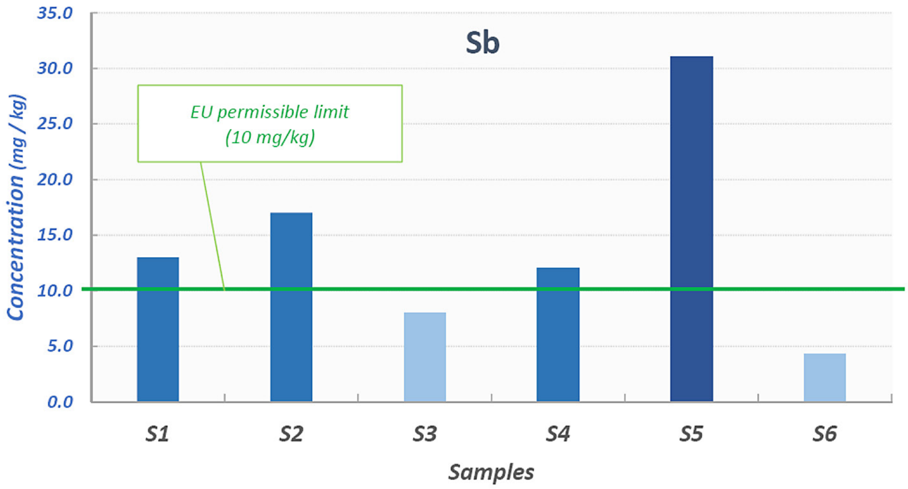


**Figure 11.** Antimony concentrations in soil samples

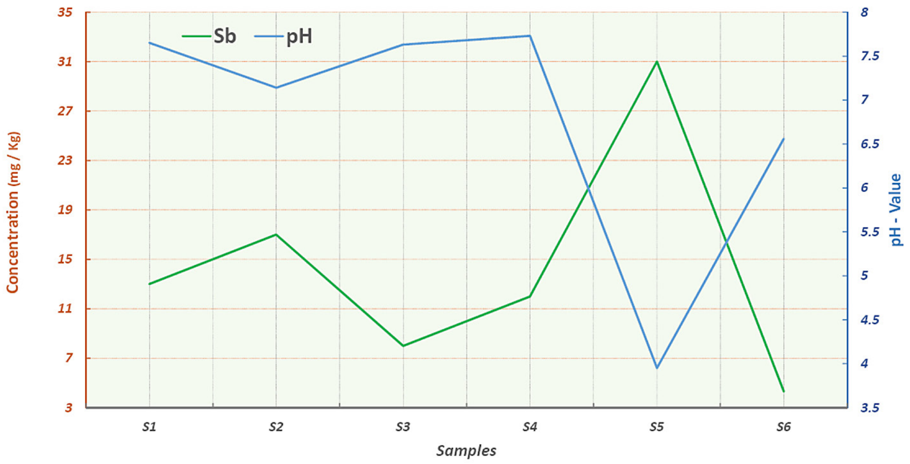


**Figure 12.** Variation in antimony content as a function of pH in soil samples

## Correlations matrix

The correlation matrix (Table 2) summarizes the relationships among Cd, Cr, V and Sb concentrations in the soil samples, providing valuable insights into their potential common sources, geochemical behavior, and environmental interactions. This analysis revealed important patterns that enhance our understanding of the behavior and possible origins of these trace elements and heavy metals in the studied soils. However, due to the limited number of samples, these findings should be considered a basis for future research.

A strong positive correlation between antimony and cadmium (r = 0.79) suggests a common anthropogenic source or similar geochemical pathways, such as industrial emissions or the weathering of sulfide minerals. In contrast, moderate negative correlations between vanadium and chromium (r = –0.43), vanadium and cadmium (r = –0.30), and antimony and vanadium (r = –0.47) indicate differences in mobility, redox behavior, or origin. Weaker correlations—such as between cadmium and chromium (r = –0.22) and antimony and chromium (r = 0.18)—highlight the complexity of heavy metal interactions in soils.

These patterns reflect a variety of contamination sources and environmental controls, likely influenced by mining activities, local lithology, pH variations, and redox conditions [3, 5, 49]. Metal behavior across sites is influenced by both anthropogenic inputs—like mining, tailings, and industrial emissions—and local geochemical conditions. While mining and tailing dump introduces metals into the environment, their mobility, retention, and interactions depend on site-specific factors such as soil mineralogy, organic matter, and redox conditions. These factors shape how metals are adsorbed, transported, or transformed, leading to distinct correlation patterns and spatial variability. Element accumulation also varied with soil pH: under acidic conditions, the accumulation trend was Cd > Sb > V > Cr, whereas under alkaline conditions, immobilization followed the order Cr > Cd > V > Sb. According to several authors, these trends are governed by redox processes, sorption onto clay minerals, complexation with humic substances, and interactions with the soil solution chemistry [13, 15, 28, 50–52].

The strong negative correlation between antimony and pH (r = –0.78) supports its increased mobility and accumulation in acidic soils. Similarly, vanadium's negative correlations with cadmium and chromium suggest that its mobility is enhanced under acidic, redox-sensitive conditions. Overall, cadmium and antimony are more soluble and bioavailable at lower pH levels, increasing their ecological risk.

## Spatial distribution

The spatial distribution of heavy metals (Cd, Cr, V, and Sb) in the study area shows a strong link between elevated concentrations and proximity to the mining waste dump and the Graçanica River (Figure 13). Cd reaches its highest levels in the southern zone, especially around sampling points S4, S5, and S6, while the lowest concentrations are recorded in the north (S1, S2), indicating limited impact there. Cr is elevated in the southwest and unexpectedly in the northeast near S1 and S2, suggesting a potential secondary source, possibly the ore zone. V is more uniformly distributed, with slight increases near S5 and S6. Sb is concentrated in the south and southeast, particularly near S4 and S5 and around the ore field. Lower concentrations of all metals—except Cr—in the northern area support the idea of localized pollution from mining activities. High total concentrations and mobility of these metals near the tailings dump, especially in agricultural soils within residential zones, pose risks to soil quality and food safety [53]. Their interaction with environmental factors can adversely affect ecosystem and human health [5, 54, 55]. Mobilized metals can accumulate in crops, leading to

**Table 2.** Correlation matrix for cadmium (Cd), chromium (Cr), vanadium (V), and antimony (Sb) concentrations in soil samples

| Parameter | Cd | Cr | V | Sb |
|---|---|---|---|---|
| Cd | 1.00 | | | |
| Cr | -0.22 | 1.00 | | |
| V | -0.30 | -0.43 | 1.00 | |
| Sb | 0.79 | 0.18 | 0.47 | 1.00 |

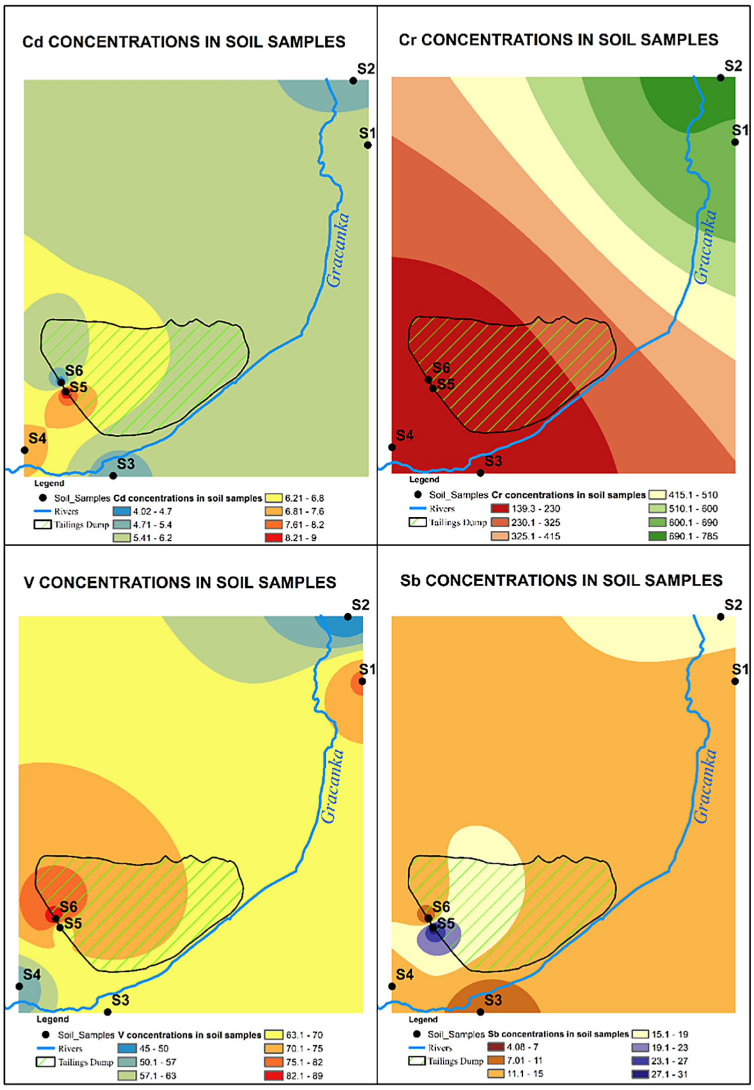


**Figure 13.** Spatial distribution of metal concentrations in soil samples

toxic effects [54–57]. Therefore, continuous monitoring and the application of physical, chemical, and biological remediation methods are essential [58, 59]. Comparative data from previous years on Cd, Cr, V, and Sb in the Gracanica region are lacking, as most prior research has predominantly focused on Pb and Zn, with limited multi-element analyses. This study establishes a foundational dataset for these lesser-studied metals, serving as a critical reference point for future environmental monitoring. Continued sampling and analysis will be essential to detect temporal changes, assess ecological risks, and evaluate the effectiveness of remediation strategies over time.

## The prospects for future research

Future research in the Graçanica area should build upon current findings on Cd, Cr, V, and Sb by analyzing their chemical speciation and bioavailability across a broader spatial extent and with a larger number of samples, to more accurately assess environmental risks. Further investigations should examine metal uptake by plants, impacts on soil microbial communities, and seasonal variations in contamination levels. Comprehensive human health risk assessments are also essential, alongside the development of predictive models, long-term environmental monitoring, and the testing of physical, chemical, and biological remediation strategies. Active community involvement and the integration of scientific findings into local policy frameworks will be critical for achieving sustainable environmental management and safeguarding both ecosystem and public health.

In complex contaminated environments—where acidic soils, mining tailings, and human exposure converge—no single remediation strategy is sufficient. A holistic approach that integrates biological methods (such as phytoremediation and microbial stabilization), chemical amendments (like lime to raise pH, or phosphates and biochar to immobilize metals), and physical interventions (targeted actions at highly contaminated hotspots) offers the most effective and sustainable solution. By reducing metal mobility and bioavailability, this multi-pronged framework not only mitigates ecological and human health risks but also promotes long-term soil restoration and environmental resilience.

## CONCLUSIONS

Heavy metal analysis in the Graçanica area reveals distinct spatial variability, with elevated concentrations of Cd, Cr, V, and Sb closely associated with the tailings dump and ore-processing zones. Cd and Sb show particularly high concentrations near the tailings, indicating localized contamination. The distribution and mobility of these metals—shaped by factors such as pH and inter-element relationships—suggest that residential areas surrounding the tailings dump are exposed to ongoing environmental risks. The bioavailability and mobility of these contaminants pose significant threats to soil quality, water resources, and food crops, especially in agricultural lands near human settlements. As a result, human exposure is progressively increasing due to persistent contamination. These findings underscore the urgent need for comprehensive research using advanced, scientifically robust methods, along with the adoption of sustainable remediation strategies to mitigate long-term ecological and public health risks posed by the tailings dump.

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