



After-effects of a closed copper mine: detailed analysis of environmental impacts in soil and plant samples

Mustafa Umut Konanç¹ · Gökçe Didar Değermenci² · İshak Afşin Kariper^{3,4} · Emine Yavuz³

Received: 4 January 2024 / Accepted: 17 June 2024 / Published online: 27 June 2024
© The Author(s) 2024

Abstract

In several countries around the world, abandoned mining sites are blighted by pollution from metal and metalloids. Generated by mining processes, toxic pollutants have lasting effects on the ecosystem. The study examined the environmental impact of waste from a copper mine that was operated by the Caucasus Copper Limited Company between 1905 and 1928, revised and commissioned by Etibank in 1936, and ceased operations 75 years ago. Soil and plant samples (needles of Scotch pine, *Pinus sylvestris* L.) were collected from five specific regions around the mine and the levels of potentially toxic elements (PTEs) were determined, including As, Zn, Pb, Cd, Ni, Mn, Cr, Cu, Al, and Fe. The data obtained were used to calculate the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), ecological risk index (ERI), human health risk index (BCF), and plant enrichment factor (EF^{Plant}). In soil samples, the average EF values of certain elements such as As (453), Cu (59.9), Pb (30.7), Zn (5.26) were detected at high levels. However, average I_{geo} values indicate high pollution levels for As (8.25), Cd (6.72), Cu (4.94), Pb (4.33) and Zn (2.42), indicating the existence of serious ecological risks in the affected areas. Additionally, the average CF values indicate serious pollution levels from heavy metals such as As (1605), Cd (584), Pb (99.4), Cu (81.9), and Zn (14.6), highlighting the extensive pollution situation resulting from mining activities. Meanwhile, average ERI values indicate that Cd, As, Cu, and Pb pose serious ecological risks in the study areas. These PTEs were found in high concentrations in the waste tail and dump. Furthermore, the analysis determined that there was enrichment for Mn, Cd, Al, Cu, Pb, and Fe elements in plant samples. These PTEs have the potential to spread more widely depending on seasonal conditions and local topography. This situation demonstrates the need to measure metal and metalloids concentrations at certain times, taking into account the potential for environmental pollution of surface runoff water and underground resources in areas with high drainage potential from acid mines, such as at the Kuvardhan mine tailings site.

Keywords Environmental monitoring · Abandoned mining · Metal and metalloids pollution

Introduction

While the mining industry makes significant contributions to a nation's economy, it also causes the emission of hazardous substances into the environment (Flores de la Torre et al. 2018). If the release of these potentially toxic elements (PTEs) is not controlled, it can result in the contamination of various environmental matrices, including soil, surface water, and groundwater. This situation poses a serious threat to the environment and public health (Hadjipanagiotou et al. 2020). Soil is one of the world's most indispensable resources and plays a fundamental role in creating vital ecosystem services by connecting natural processes (Khan et al. 2022). Soil quality is generally defined as "the capacity of a soil to function within characteristic or controlled

✉ Mustafa Umut Konanç
umutkonanc@artvin.edu.tr

✉ Gökçe Didar Değermenci
gdegermenci@kastamonu.edu.tr

¹ Artvin Vocational School, Laboratory Techniques, Artvin Çoruh University, Artvin 08100, Türkiye

² Department of Environmental Engineering, Faculty of Engineering and Architecture, Kastamonu University, Kastamonu 37100, Türkiye

³ Department of Science Educations, Faculty of Education, Erciyes University, Kayseri 38039, Türkiye

⁴ Erciyes Teknopark, Building Number 1, No. 41, Kayseri 38039, Türkiye

environmental limits, provide ecosystem services, maintain plant and animal productivity, protect or enhance water, and support human health and habitat.”(Golia 2023), Anthropogenic activities such as mining, steel industry, waste incineration (including sludge processing management, control of acid discharges and ashes) and poor management of electronic waste (e-Waste) deteriorate soil quality by causing uncontrolled introduction of metals and metalloids into the soil (Quintero-Payan et al. 2024). Metal and metalloids-related soil and water contamination have become a significant problem in many regions of the world (Khafouri et al. 2021). The release of metal and metalloids into the soils of mining areas and their surroundings leads to significant increases in their concentration, with devastating effects on the ecosystem’s function and structure (Cheng et al. 2022).

Many metal and metalloids, including Zn, Cu, and Se, are necessary for the regular development of plants and other living things. Other metals that are not basic elements, such as Pb or Cr, can be tolerated by the ecosystem at low concentrations, but these metal and metalloids can become toxic at higher concentrations (Srinivasa Gowd et al. 2010). Indeed, metal and metalloids pollution from mines is considered to be a contributing factor to deforestation (Sousa et al. 2012) and reduced biodiversity and aesthetic appearance of forests, and they cause economic losses as these areas tend to lose their suitability for agriculture (Pehlivan et al. 2021). Therefore, the determination of soil pollution levels and the assessment of metal and metalloids pollution in abandoned mines are important environmental issues (Loska et al. 2004).

Mining operations can cease for multiple reasons, including increasing costs, depleting reserves, shifting ore grades, environmental effects, and geological causes (Horasan et al. 2021). Damage to the environment can continue to occur even many years after mine closure, and indeed this is being recognized as one of the main sources of pollution worldwide. These abandoned sites are a source of environmental pollution from high levels of metal and metalloids with toxic effects on surface waters, living organisms, and soils (Beane et al. 2016). Waste from copper (Cu) mines may contain other elements besides Cu, such as As, Cd, Co, Cr, Mn, Ni, Pb, and Zn, all at various concentrations depending on the mining method that was used (Karczewska et al. 2015). These elements accumulate in the soil and are transferred to the plant by the plant’s roots. In polluted areas, the leaves of tree species are considered to be accumulation monitors, in which significant amounts of metal and metalloids and other pollutants accumulate on the leaf surface (Madejón et al. 2006). Pine trees, especially their needles, can be used to measure metal and metalloids pollution in the environment (Pająk et al. 2015). Long-lived organisms, such as trees, can grow in soil with high metal and metalloids concentrations

due to resistance mechanisms, including ectomycorrhizal symbiosis. As a result, the Scotch Pine (*Pinus sylvestris* L.) and Silver Birch (*Betula pendula* Roth.) are the species most frequently used on polluted soils in Eastern Europe (Bierza et al. 2020). Scotch pine is characterized by the fact that it easily assimilates various elements and has a lower tolerance to environmental pollution compared to other conifers. Scotch pine is considered a useful bioaccumulator and model tree for pollution monitoring studies (Klink et al. 2018). Such trees are useful because high concentrations of metal and metalloids adversely affect soil quality and destroy functional ecosystems, resulting in otherwise barren lands devoid of vegetation (Chileshe et al. 2020).

For the past decade, the USEPA (United States Environmental Protection Agency) model has been widely used in assessing the health risk of soils in the vicinity of copper mines (Chen et al. 2022). For this reason, it is necessary to determine the levels of these PTEs to determine the environmental effects of abandoned mining sites and to take precautionary measures (Covre et al. 2022). The enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), ecological risk index (ERI), pollution load index (PLI), and human health risk index, as well as various indices such as bioconcentration factors (BCFs), were used to evaluate the potential pollution level of these PTEs in soil and plants (Hakanson 1980; Men et al. 2018; Ferreira et al. 2022; Steingraber et al. 2022; Bayraklı et al. 2023).

Metal and metalloid contamination in soil associated with mining activities is a major problem worldwide. Abandoned mine sites are associated with environmental risks and mining waste has been uncontrolled. A case study was conducted at the Jerada coal mine site in Morocco and soil and coal mine waste rock were sampled. The results show that coal mine waste rock is associated with soil contamination (Khalil et al. 2023). Another study evaluated trace element contamination in soils and stream sediments at an abandoned traditional gold mining site in Cameroon. Analyses of samples collected from the surrounding area of the abandoned mine site used geochemical background and geo-accumulation indices to discriminate between natural and anthropogenic enrichment. As a result, the abandoned mine site was found to be the main source of soil and stream sediments with high levels of cadmium, lead and zinc, which may be hazardous to human health (Paternie et al. 2023). Another study investigated the levels and sources of heavy metal pollution around the Selibe Phikwe copper mine. It was found that the area was moderately polluted with heavy metals. However, it was emphasized that this pollution could increase in the future and cause serious impacts on the soil environment and food chain (Motswaiso et al. 2019). Similarly, research from around the world shows that

mining activities increase concentrations of metals and metalloids in soils, resulting in environmental impacts.

Copper mining has a long history in Türkiye. Artvin province, located in the east of the Eastern Black Sea metallogenic mineralization, is an extremely important region for metallic mines. Artvin Kuvarshan copper mine, which was among the very first copper mines to operate in Türkiye, was first developed by the German company B. Simens in 1905. Suspending its activities in 1917, the enterprise was revisited by Citibank in 1937 and a total of 232,800 tons of ore was extracted, with 8815 tons of pure copper production, between 1937 and 1941. It was finally closed in mid-1945 due to the depletion of reserves.

There are two types of mineralization in the Kuvarshan copper mine, which is located in the east of the Çoruh region and has vein-type mineral reserves. The first type of mineralization is located in the upper part and is defined as poor pyritic mineralization (gelberze). Containing 1.5% Cu, this ore structurally contains pyrite, chalcopyrite, and galena. The second type of mineralization is located below and is defined as copper-rich mineralization (grauerze). Containing 6–7% Cu, this ore is structurally composed of chalcopyrite, bornite, neodigenite, chalcocite, sphalerite, and secondary galena and tennantite (Kovenko 1942). The ore extraction process in the mine site was carried out through closed galleries and processed in the smelting facility of the enterprise, where blaster copper production was carried out (Dogangün Yasa and Yardımcı 2022).

In general, the effects of abandoned mining sites on the environment have been studied in Kuvarshan. Many

previous studies have examined its high concentrations in water and mine waste in abandoned mine sites. However, to date, soil and vegetation pollution around abandoned mine sites has not been adequately investigated due to a lack of accurate data and information. In fact, understanding the sources and characteristics of mine pollution in Kuvarshan may provide useful information for the implementation of rehabilitation projects for abandoned mines and assist decision-makers in the development of new policies for the remediation of mines.

The abandoned mining site in Kuvarshan was chosen to evaluate the impact of mining activities on the surrounding soils and vegetation. The objectives of this study are as follows: (1) geochemical and mineralogical characterization of soil samples; (2) the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), ecological risk index (ERI), human health risk index (BCF), and plant enrichment factor (EF^{plant}) values of selected chemical elements in soils and (3) determination of plant accumulation indexes in plant samples.

Materials and methods

Data collection

Research articles in recent years have mentioned the presence of toxic elements in most samples from soils near copper mines. These include Cu, As, Zn, Pb, Cd, Ni, Mn, and Cr. These elements are in the priority pollutant class, as determined by the USEPA, and can accumulate in the topsoil through both natural and anthropogenic sources (Xiao et al. 2020). Here, samples were collected from the abandoned Kuvarshan copper mine in the east Black Sea region of Türkiye (41° 14' 986" N). In this study, the environmental effects of the wastes of the mine site in an area of approximately 2088 m² were analyzed by dividing the area into 5 different regions. In this context, the landfill was assumed as the center and 4 pollution zones (regions 1–4) were defined according to their distance to the area and the geological structure. A fifth region was designated as a control area. A total of 41 (40 point + 1 control) soil and 33 (32 point + 1 control) soil-related Scotch pine samples were collected from each of the regions, using a random sampling model (Table 1; Fig. 1).

Analysis of plant and soil samples

Soil samples collected from the field were dried for 10 days until they were air-dry and homogenized by passing through 2 mm sieves. Classification of soil samples by particle size was conducted using the Bouyoucos hydrometer method,

Table 1 Groupings of abandoned mine site study area

Region	Color code	Sample codes (soil)	Sample codes (plant)	Total number of samples of soil	Total number of samples of plants
1	Green	34, 35, 36, 37	-	4	-
2	Brown	1, 9, 10, 12, 14, 15, 17, 19, 22, 25, 29, 31, 33, 38	1, 9, 10, 12, 15, 17, 19, 22, 25, 29, 31, 33	14	12
3	Yellow	4, 5, 8, 11, 13, 16, 18, 20, 21, 23, 24, 26, 28, 30, 32	4, 8, 11, 13, 16, 18, 20, 21, 23, 24, 26, 28, 30, 32	15	14
4	Blue	2, 3, 6, 7, 27, 39, 40	2, 3, 6, 7, 27, 39	7	6
5 (control)		41	41	1	1

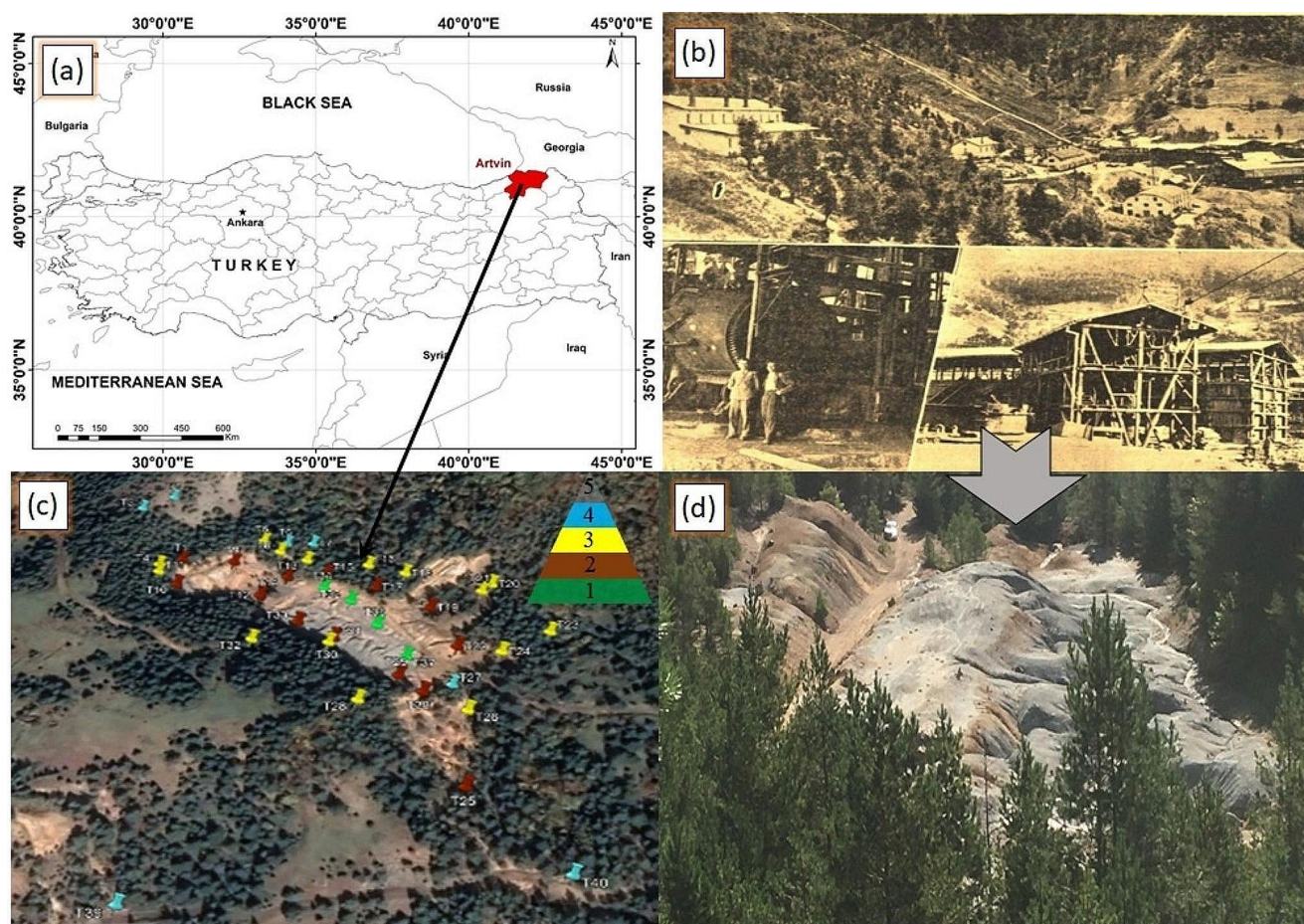


Fig. 1 a) The location of the study area, b) photograph of the Kuvavshan smelter, c) study area and d) mineral dacite and waste heap waste area

Table 2 Digestion methods and metal determination with ICP-OES

Sample type	Sample preparation steps	Microwave digestion	Methods
Soil	0.5 g Soil + 9 mL HNO_3 + 3 mL HCl	Heat to 175 ± 5 °C with a ramp time 5.5 min and hold 4.5 min	(Element 2007)
Plant	0.3 g plant + 2 mL HNO_3 + 3 mL H_2O_2	Heat to 145 ± 5 °C with a ramp time 5.5 min and 180 ± 5 °C hold 10 min	(Konanç 2021)

pH and conductivity measurements by the 1:2.5 soil water suspension method, total lime using a Scheibler calcimeter, and aggregate stability (AS) by the wet sieve method (Fernández-Caliani et al. 2009).

The plant samples (leaves and needles) collected in the field were washed three times with distilled water, clearing particles from them, and dried at 60 °C for 48–60 h until they reached a constant weight. The weighed plant samples were homogenized by pounding with a pestle and stored at 4 °C until analysis (Dary et al. 2010).

Soil and plant samples prepared for multi-elemental analysis using inductively coupled plasma optical emission

spectroscopy (ICP-OES; Perkin Elmer Optima 8000) were weighed in different amounts, placed in Teflon containers, and extracted by applying the microwave decomposition method (Table 2).

After the degradation process, a 1 mg/L internal standard (Yttrium) was added to all samples, and the final volume was supplemented to 50 mL. Metal concentrations (As, Zn, Pb, Cd, Ni, Fe, Mn, Cr, Cu, and Al) in soil and plant extracts were analyzed using ICP-OES. Standard deviations were determined from three replicates of each sample. In addition, arsenic in plant samples was determined by hydride production and ICP-OES (Masson et al. 2006).

Analytical procedure

This procedure was used to determine its validity for the quantitative analysis of metal ions in plant material and soil. Optimization studies for the procedure were performed through precision or reproducibility, and calculation of relative standard deviation and limits of detection (LOD) and quantification (LOQ).

To determine the accuracy of soil and plant samples, standard reference materials CRM027 (Sandy Loam 10) and ERM-CD281 (Rye Grass) were used in accordance with environmental conditions, metal and metalloids contents, and texture. The values given for both standard reference materials were compared with the certificate values, and the accuracy of the method was given in Table 3 together with the recovery percentages. In addition, the LOD (the smallest concentration of the analyte) and LOQ (the smallest concentration at which the analyte is quantified) were calculated according to the International Union of Pure and Applied Chemistry (IUPAC) for the method used in the study. According to this method, LOD and LOQ values for each metal were obtained by multiplying the standard deviation of the method blank measurements by 3 and 10, respectively (Thompson et al. 2002). However, the matrix effect that may occur during the measurements was minimized by using the internal standard Yttrium (Masson et al. 2006).

Results of precision and accuracy analyses

According to the obtained results, the recovery values for each metal were found to be between 80 and 120%, demonstrating the accuracy of the method (Shabanda et al. 2021). Additionally, repeatability or precision was determined by calculating the relative standard deviation, which was found to be below 10% for all the metals. These results indicate the suitability of the selected extraction method in terms of precision and accuracy within a 95% confidence interval (Table 3).

Statistical analysis

Analysis of all data was carried out using SPSS version 26.0. Since the variances of the soil and plant samples were

not homogeneous, the differences between the groups were compared using the Kruskal-Wallis test, and the relationship between the physical and chemical analytes and the metals was tested using Spearman-Brown correlation analysis.

Soil pollution and risk assessment indexes

In order to evaluate the metal and metalloids (As, Zn, Pb, Cd, Ni, Fe, Mn, Cr, Cu and Al) pollutions measured as a result of the analysis of topsoil (0–30 cm) samples collected from 40 points, enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), ecological risk index (ERI), human health risk index has been calculated. The detailed information is given as supplementary material.

Determination of plant element uptake and bioaccumulation performance

Plant samples were collected from 33 points in the abandoned mine site. Bioconcentration factor (BCF) and plant enrichment factor (EF^{Plant}) were calculated in these plant samples. The formulae used in the calculations are provided in the supplementary material.

Results and discussion

Physicochemical properties of soils

The physicochemical properties of soil samples taken from 40 points near the Kuvarshan abandoned mine site and natural forest are given in Fig. 2 and supplementary Table S1. According to these data, at the 0–30 cm depth, the sand content ranged from 47.16 to 97.9%, the clay content between 0.04% and 29.71%, the silt content between 0% and 49.7%, and the aggregate stability values between 23%

Table 3 Accuracy and precision of metal and metalloids

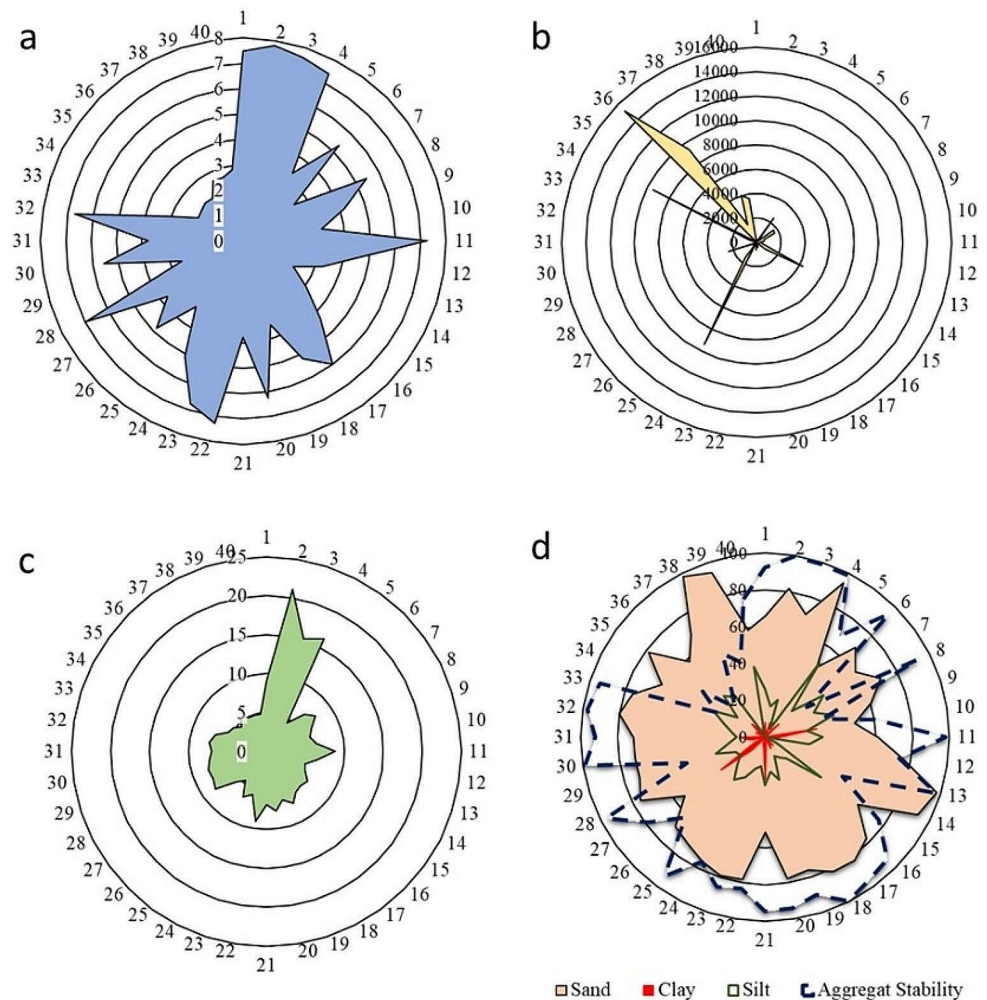
Metals	SRM** (Soil 027)	EMC*** (mg/kg)	% Recovery soil	SRM** (Plant ERM CD-281)	EMC*** (mg/kg)	% Recovery plant	LOD (mg/kg)	LOQ (mg/kg)
As	59.0±0.93	50.3±0.4	85.22	42±0.01	n.d.	-	0.0105	0.035
Zn	590±9.75	608.1±0.29	103.05	30.5±1.1	29.60±0.91	97.04	0.001	0.004
Pb	276±4.59	194.1±1.20	70.32	1.67±0.11	1.76±0.31	105.83	0.008	0.028
Cd	98.7±1.64	108.3±1.13	109.72	0.120±0.007	0.145±0.018	120.08	0.008	0.028
Ni	298±5.20	270.6±1.55	90.60	15.20±0.6	n.d.	-	0.001	0.004
Mn	837±18.9	804.8±1.82	96.05	82±4	83.56±0.75	101.90	0.003	0.033
Fe	6980±1.42	5430±49.71	77.79	180	190.02±0.08	105.55	0.008	0.026
Cu	89.6±1.66	81.4±1.29	90.84	10.2±0.5	11.03±0.17	108.13	0.002	0.007
Cr	240±3.82	235.6±2.58	98.16	24.8±1.3	26.68±0.27	107.58	0.0006	0.002
Al	6780±499	8170.6±253.6	120.50	-	32.65±1.43	-	0.001	0.011

*nd: Reference value not certificated or not detected

**Standart Reference Materials (SRM)

***Extractable Metal Content (EMC)

Fig. 2 **a)** The pH of the collected soil samples, **b)** electrical conductivity, **c)** CaCO_3 and **d)** texture content in soil of the abandoned Kuvarshan mine area



and 99.81%. The dominant soil texture was sandy loam. The values of sand, clay, and silt found in this study were similar to those found in other mine waste sites by previous studies (Zhen et al. 2019). Soil aggregate size distribution and stability measurements are considered to be indicators of soil quality. The value of aggregate stability is an important factor in determining the susceptibility to erosion: as the aggregate stability value increases, the resistance to erosion also increases (Yakupoğlu et al. 2015). The pH of the collected soil samples generally exhibited acidic characteristics (range = 2.01–7.79; mean = 4.48). The pH is one of the most important properties that affect the presence, persistence, and mobility of PTEs in mining areas. Low pH values are common in Cu mining wastes, that are rich in sulfide minerals and that release PTEs under oxidizing conditions (Covre et al. 2022). Electrical conductivity values varied from 7.88 to 15,250 $\mu\text{S cm}^{-1}$, with a mean of 1902 $\mu\text{S cm}^{-1}$, showing high salinity. The CaCO_3 values of the collected soil samples ranged between 5 and 21, which are the average limit values (Fig. 2-c), indicating moderately calcareous soils.

Soil structure plays an important role in managing biological and physical processes. In this regard, soil with a stable structure exhibits high erosion resistance. Aggregates are one of the fundamental structural elements of soil and play an important role in soil function (Shen et al. 2022). Findings from monitoring studies, especially those tracking the environmental behaviour of trace metals, should not be limited to bulk soil alone, but should also focus on the aggregate level. Moreover, the composition and stability of aggregates can influence the accumulation of heavy metals in bulk soil. Previous studies have shown a strong relationship between aggregate particle size and heavy metal content. For example, in a rice field in southern China, coarse sand-sized soil aggregates were found to have the highest heavy metal content (Chen et al. 2014). To date, few studies have investigated the distribution behaviour of metal elements in aggregates from different mine soils. Therefore, in this study we investigated the distribution of soil trace metals in different soil areas using aggregate stability, texture and trace metals.

The metal and metalloids concentrations in the soils affected by the abandoned mining site are shown in supplementary Table S2. These samples have decreasing metal and metalloids concentrations, in the following order: $\text{Fe} > \text{Al} > \text{As} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Mn} > \text{Cd} > \text{Cr} > \text{Ni}$. In a study by Demiray (2017), the geological structure of the Kuvarshan mine flotation waste site (region 1) was determined using ore microscope, X-ray diffraction (XRD), and X-ray fluorescence devices. The findings showed that the flotation waste consisted mostly of pyrite (FeS_2) and heavy amounts of chalcopyrite (FeCu_2S). Additionally, XRD analysis revealed differences between the major components of the flotation waste (calcite, jarosite) and those of the host rock (quartz, muscovite). Moreover, the average values of As (4.91 g/kg), Pb (2.81 g/kg), Fe (141 g/kg), and S (64 g/kg) were determined (Doğrul Demiray 2017). Examination of the average values shows that the metal and metalloids concentrations in the soil exceed the permissible limits set by the Regulation on the Control of Soil Pollution and Point Source Polluted Sites, published by the Ministry of Environment and Forestry in 2010 ($\text{Pb} = 50\text{--}300$, $\text{Cd} = 1\text{--}3$, $\text{Ni} = 30\text{--}75$, $\text{Cr} = 100$, $\text{Cu} = 50\text{--}140$, $\text{Zn} = 150\text{--}300$ mg/kg) (CSB 2010). Iron, which was the fourth most abundant element in the soil structure, is mostly present in forms that plants cannot take up. The total Fe content in the collected soil samples varies between 32,713 and 272,533 mg/kg, with an average of 96,746. Typically, the Fe content in soils is between 1 and 5% ($1\text{--}5 \times 10^4$ mg/kg). However, most of this ratio is not available for plant uptake (Tuğba et al. 2021). The total Mn values in the soil samples collected from the study area were determined to be between 17 and 1384 mg/kg, with an average of 374, which exceeds the limit value of 70 mg/kg. The element manganese plays an important role in chlorophyll synthesis and nitrogen absorption in plants and can lead to Fe deficiency (Tuğba et al. 2021). Figure 2 and Table S2 show that the pH, conductivity, total lime, and metal and metalloids concentrations of the soil samples taken from different regions were arranged in the following order (from lowest to highest): Regions $1 < 2 < 3 < 4 < 5$. These findings can be explained by the oxidation of pyrite in the geological structure of the site, leading to the release of sulfate (SO_4^{2-}).

Pollution levels and risks of selected PTEs

Variations in metal and metalloids enrichment factor (EF), geo-accumulation index (I_{geo}), and contamination factor (CF) in the Kuvarshan mine area

EF values were calculated so that it was possible to differentiate the anthropogenic effects from natural sources for PTEs in soil samples taken from the Kuvarshan mining area

and its surroundings (Fig. 3). The mean EF values of the elements indicate that As (453), Cu (59.9), Pb (30.7), Zn (5.26), Cd (1.02), Cr (0.86), Ni (0.65), Mn (0.41), and Al (0.06) are all found at enriched levels (Fig. 3). The excessive enrichment of As and Cu, very high enrichment of Pb, significant enrichment of Zn, and an indication of extremely high soil pollution levels, can all be observed. However, there was only slight enrichment for Cd, Cr, Ni, Mn, and Al. According to these findings, the presence of high concentrations of As, Cu, and Pb can be explained by the pyrite and tennantite minerals involved in the ore formation at the Kuvarshan mining area (Doğrul Demiray 2017). It has previously been noted that contamination is likely to be anthropogenic when EF values are greater than 1.5 (Zhang and Liu 2002). Soil samples taken from copper mining areas and their surroundings have previously been reported to contain high concentrations of various metals, including Cu, Pb, Zn, Cd, and As (Verdejo et al. 2015). In a study by Gök (2008), the Artvin report (dated 1921) was examined in detail and it was found in the report that the Kuvarshan factory area was only operated in the winter months to prevent harm to plants and trees in the factory area from As. These results indicate that anthropogenic release of As, Pb, and Cu into the environment may have been possible since at least 1921 (Gök 2008).

To evaluate the pollution levels of As, Cu, Pb, Zn, Cr, Cd, Ni, Mn, Fe, and Al in surface soils collected from 40 sites, Igeo values were calculated (Fig. 4). The average Igeo values of the elements in the mine site were determined as extremely highly polluted for As (8.25) and Cd (6.72), highly to extremely polluted for Cu (4.94) and Pb (4.33), moderately to highly polluted for Zn (2.42), and unpolluted to moderately polluted for Fe (0.77), while no pollution was determined for Cr, Ni, Mn, and Al. High levels of these eight metal and metalloids have also been found in soil samples from copper mining sites across the world. According to the average Igeo scales, Cu pollution levels were extremely high in Australia, Italy, Oman, Peru, the United Kingdom, and Zambia, while Cd pollution levels were higher in other areas of the study sites in Australia, China, Russia, and the United Kingdom. The highest pollution levels in soils near Cu mines were found in Morocco for Mn (2.04), in Chile for As (6.27), in Italy for Cr (3.55) and Ni (4.24), and in the United Kingdom for Pb (7.57) and Zn (3.30) (Chen et al. 2022). Therefore, we can conclude that soil pollution with high levels of As, Cd, Cu, Pb, and Zn in and around the mining site may be plausibly attributed to the copper mining activities in the region.

CF values were also calculated to assess the pollution levels of As, Cu, Pb, Zn, Cr, Cd, Ni, Mn, Fe, and Al in soil samples collected from an abandoned mining site (Fig. 5). The average CF values for PTEs indicate very high pollution

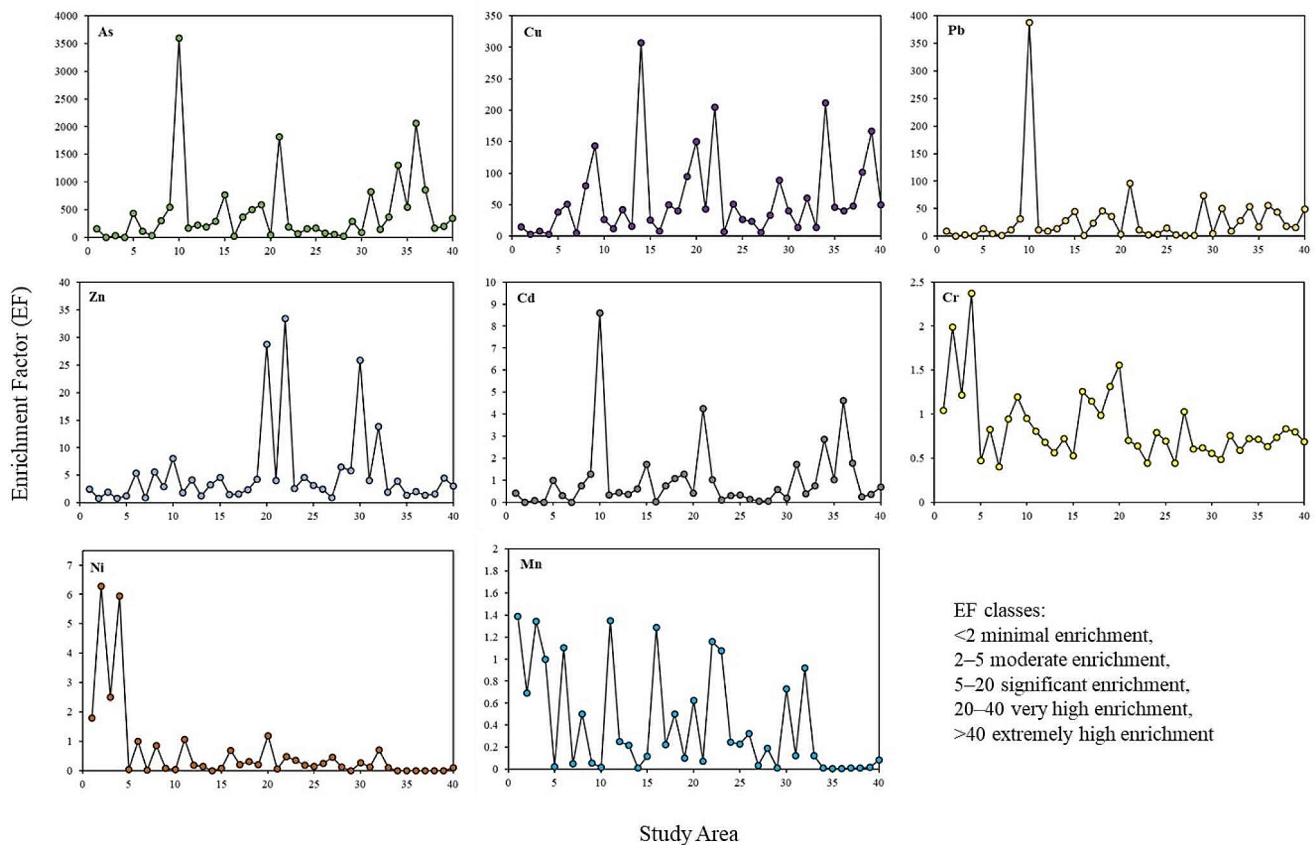


Fig. 3 Metal and metalloids enrichment factor of Kuvarshan mine area

for As (1605), Cd (584), Pb (99.4), Cu (81.9), and Zn (14.6), moderate pollution for Fe (3.13) and Cr (1.18), and low pollution for Ni (0.94), Mn (0.71), and Al (0.17). Although the metal and metalloids pollution levels in the mining site are in the same category, their magnitudes vary depending on the type of waste. Based on the average CF values, As is the most dominant pollutant in samples from the site, followed by Cd, Pb, Cu, Zn, Fe, and Cr.

The Pollution Load Index (PLI) is an indicator of the overall multi-element pollution in an area. Therefore, a higher PLI indicates that an area is contaminated with multiple sources of PTEs collectively. Sampling points in any location with PLI values greater than 1 indicate that the points are deteriorating (Tomlinson et al. 1980). High concentrations of As, Cd, Cu, Pb, Zn, Fe, and Cr values in CF values contribute to the increase in PLI values (Fig. 6). This confirms that there is significant contamination at the sampled locations.

Ecological risk index (ERI)

ERI and potential ecological risk index (PERI) values were calculated to assess the ecological risks caused by eight metal and metalloids (As, Cu, Pb, Zn, Cr, Cd, Ni, and Mn)

that were detected in soil samples from the abandoned mining site and its surroundings (Fig. 7). When the average ecological risk values of these eight metal and metalloids were calculated individually, they were found to decrease in the following order: Cd (17,334) > As (16,053) > Pb (497) > Cu (410) > Zn (14.6) > Ni (4.70) > Mn (3.55) > Cr (2.35). The average ERI values for Cd, As, Cu, and Pb were found to exceed 320, which indicates a serious ecological risk. In previous research of soils near Cu mining sites, Cu, Cd, and As were identified as priority control pollutants, and it was argued that various strategies should be designed to manage and remediate this contamination (Chen et al. 2022). The average ERI values for Zn, Ni, Mn, and Cr were below 40, and as a consequence, their low ecological risk is not shown in Fig. 7.

The average PERI value was calculated to be 34,319, which indicates a significantly high potential risk around the copper mine because this exceeded 600. As shown in Fig. 7, Cd and As were the biggest contributors to this PERI value. Cd, in particular, has a high toxicity potential for living organisms due to its high solubility and accumulation under physiological conditions (Carvalho et al. 2021). The toxic-response factors of Cd (30), As (10), Pb (5), and Cu (5) were significantly higher than that of other metal and

Fig. 4 Metal and metalloids geo-accumulation index (I_{geo}) of Kuvvarshan mine area

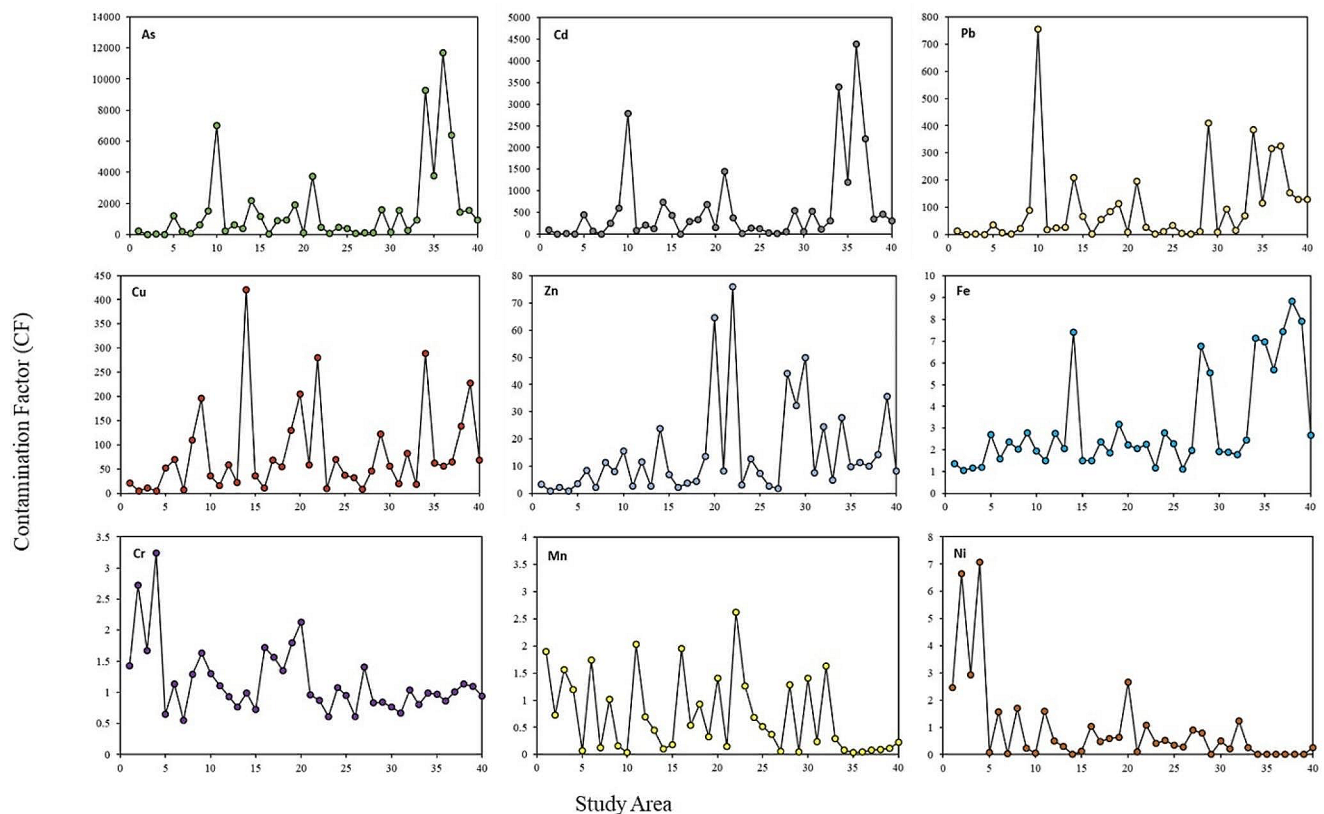
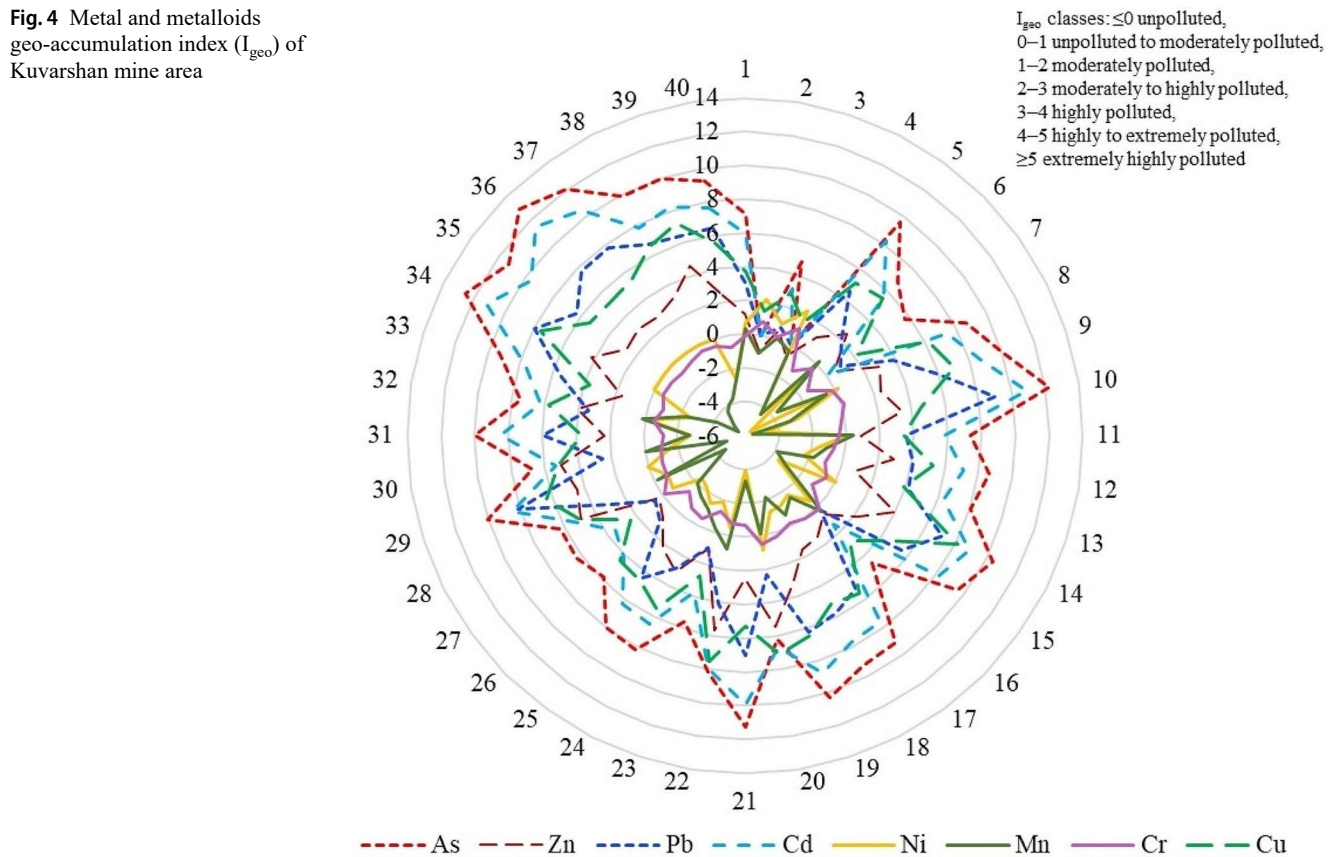


Fig. 5 Metal and metalloids contamination factor (CF) of Kuvvarshan mine area

Fig. 6 Metal and metalloids pollution load index (PLI) of Kuarvarshan mine area

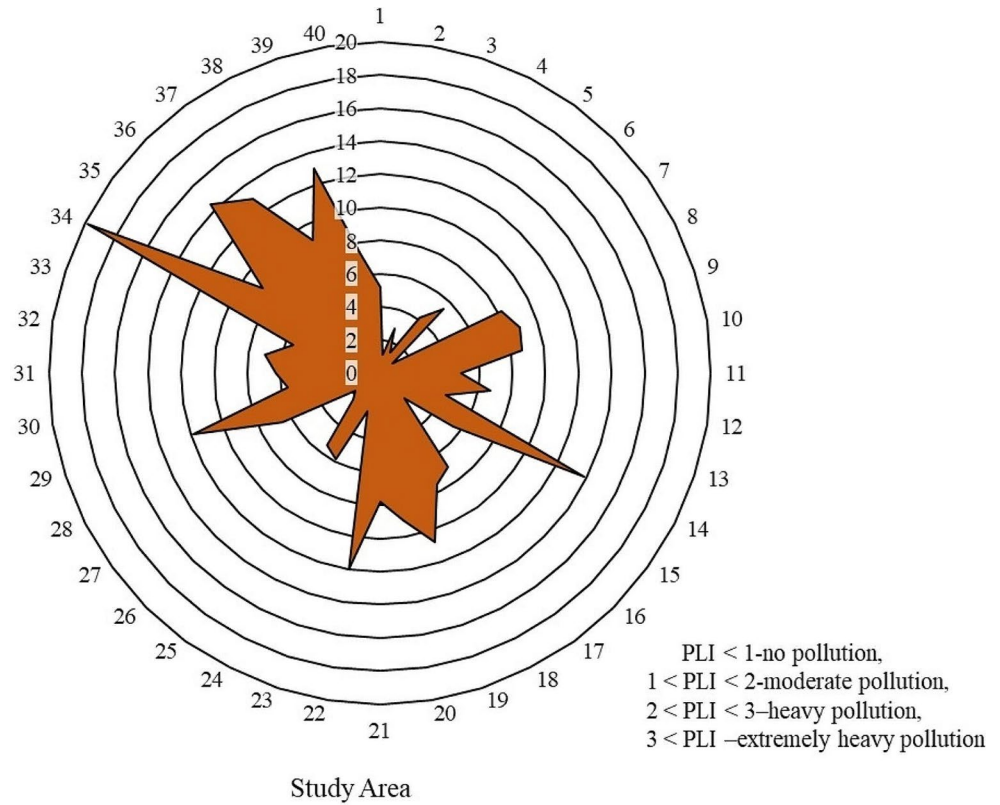
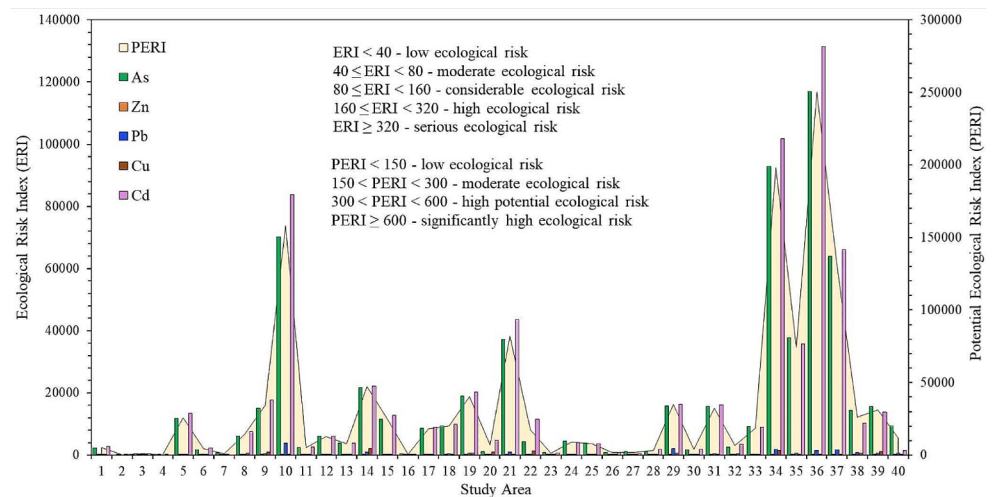


Fig. 7 Metal and metalloids ecological risk index (ERI) and potential ecological risk index (PERI) of Kuarvarshan mine area



metalloids (Chen et al. 2022). In copper mining, especially in open pit operations, high concentrations of metal and metalloids (As, Cd, Cu, and Pb) are present, which pollute the soil as a result of the wind spreading fine particles into the atmosphere, thus becoming an important source of particulate matter (Punia 2021).

Human health risk index

The concentrations of metal and metalloids including As, Cu, Ni, Pb, and Zn in soil were used to optimize human

health risks at the mining site. The average daily doses (ADD), the non-carcinogenic hazard coefficient (HQ), hazard index (HI), and the potential carcinogenic risk (CR) levels were calculated based on exposure through ingestion, dermal contact, and inhalation of the elements from soil samples collected for assessing human health risk, as shown in Table 4. When HI values were evaluated for As and Pb in the study area (for both adults and children), values greater than 1 indicate that more attention should be paid to these elements due to non-carcinogenic risk. The CR values for As were significantly higher than the acceptable maximum

Table 4 Metal and metalloids in different exposure of health risk of Kuvarshan mine area

		ADD						HQ						CR					
		Ingest			Inhalation			Ingest			Dermal			Inhalation			Ingest		
		Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult
As	Adult	4.40E-03	2.96E-04	6.47E-07	1.47E+01	2.40E+00	1.51E-01	1.72E+01	8.85E-04	5.95E-05	1.31E-08	9.45E-04							
	Child	4.10E-02	9.01E-04	1.15E-06	1.37E+02	7.33E+00	2.67E-01	1.05E+03	8.26E-03	1.81E-04	2.32E-08	8.45E-03							
Zn	Adult	1.04E-03	2.33E-06	1.53E-07	3.47E-03	3.89E-05		3.51E-03											
	Child	8.15E-04	7.11E-06	2.71E-07	3.47E-03	3.89E-05		2.83E-03											
Pb	Adult	2.32E-03	5.19E-06	3.41E-07	1.65E+00	9.90E-03		1.66E+00	1.97E-05		1.43E-08	1.97E-05							
	Child	2.16E-02	1.58E-05	6.04E-07	1.54E+01	3.02E-02		1.55E+01	1.84E-04		2.54E-08	1.84E-04							
Cd	Adult	8.16E-05	1.83E-07	1.20E-08	8.16E-02	7.32E-03		9.31E-02											
	Child	7.62E-04	5.58E-07	2.13E-08	7.62E-01	2.23E-02		7.92E-01											
Ni	Adult	2.39E-05	5.36E-08	3.52E-09	1.20E-03	9.93E-06		1.25E-03	4.07E-05	2.28E-08	2.96E-09	4.07E-05							
	Child	2.23E-04	1.64E-07	6.24E-09	1.12E-02	3.03E-05		1.13E-02	3.80E-04	6.95E-08	5.24E-09	3.80E-04							
Cr	Adult	5.64E-05	1.27E-07	8.30E-09	1.88E-02	4.22E-03		2.30E-02	2.83E-05	2.53E-08	3.49E-09	2.83E-05							
	Child	5.27E-04	3.86E-07	1.47E-08	1.76E-01	1.29E-02		1.88E-01	2.64E-04	7.71E-08	6.18E-09	2.64E-04							
Cu	Adult	1.61E-03	3.60E-06	2.36E-07	4.01E-02	3.00E-04		4.04E-02											
	Child	1.50E-02	1.10E-05	4.19E-07	3.75E-01	9.14E-04		3.75E-01											

values for both adults and children, while those for Pb, Ni, and Cr exceeded the acceptable maxima for children. Thus, the soil in the study area appears to have a high potential carcinogenic risk for As, Pb, Cr, and Ni. However, as the site is a forested area and not used for agricultural purposes, these risk levels are not expected to be very high.

Plant accumulation index

The biological accumulation of PTEs was investigated in samples taken from the needles of Scotch Pine trees. The average values of these PTEs in the pine needle samples were determined as follows: Mn (645 mg/kg) > Al (393 mg/kg) > Fe (245 mg/kg) > Zn (51.7 mg/kg) > Cu (5.30 mg/kg) > As (4.79 mg/kg) > Pb (2.63 mg/kg) > Cr (1.19 mg/kg) > Cd (0.37 mg/kg). The concentration of Mn in the plant samples taken from the site ranged between 42.5 and 2524 mg/kg, with an average value of 645. These values were higher even than areas affected by traffic, according to data from several previous studies (Çomaklı and Bingöl 2021). The impact of former mining seems to be the most likely explanation for this high value. The soil samples taken from the unpolluted area of the mine site showed the following order of concentrations: Fe (19,277 mg/kg) > Al (3,958 mg/kg) > Mn (458 mg/kg) > Zn (40.5 mg/kg) > Cu (23.5 mg/kg) > As (21.3 mg/kg) > Cr (18.8 mg/kg) > Cd and Pb (not detected), while the Scotch pine needle samples taken from the same unpolluted area showed the following order: Fe (69.0 mg/kg) > Al (51.4 mg/kg) > Zn (43.9 mg/kg) > Mn (19.8 mg/kg) > Cr (1.46 mg/kg) > Cu (1.14 mg/kg) > Pb (0.71 mg/kg) > Cd (0.05 mg/kg).

Metal and metalloids play a crucial role in plant growth, but their high concentrations can have toxic effects on plants. The highest metal and metalloids value measured in the pine needle samples taken from the contaminated site (i.e., Mn), was approximately 32.6 times higher than the value measured in the unpolluted site. In a study by Demiray (2017), the percentage leachability of waste dump heaps was determined by the humidity cell test. According to the findings of this study, Mn was the most leachable metal in the site, with a percentage of 57%, which may explain why the manganese level was so high in the site (Doğrul Demiray 2017). According to some sources, the high value of Mn is associated with an increase in Mn levels in shoots and roots during plant growth. Therefore, Mn concentration in plants is an important factor for plant development (Khan et al. 2021). The critical levels of Mn for most plants range from 15 to 25 mg/kg, while the toxic concentration of Mn in plants varies depending on both plant and soil factors. Generally, most plants are affected when Mn content lies above 400 mg/kg. It can also be observed that the soil composition of the unpolluted site has high Al and Fe. The Al and Fe

ratios in the pine needle samples taken from the polluted and unpolluted sites were 7.64 and 3.56, respectively. Mn, Al, and Fe accumulate in the soil at low pH values, and high values of these parameters are interrelated (Kabata-Pendias 2004). In a previous study, the accumulation properties of needles were investigated (specifically regarding Mn, Fe, Cu, Ni, Zn, and Cd), and relatively high contents of Fe, Mn, and Zn were detected in the needles of some *Pinus* species (Parzych et al. 2017).

To determine the enrichment factor for the Scotch pine tree, a control plant sample was taken from the uncontaminated area of the Kuvarshan mine site. The EF^{Plant} value is considered to indicate enrichment if it is greater than 2 (Parzych and Jonczak 2014). When the average EF^{Plant} values of the samples taken from the study area were ranked, they were calculated as Mn (32.6) > Al (7.64) > Cd (6.85) > Cu (4.64) > Pb (3.71) > Fe (3.56) > Zn (1.18) > Cr (0.82) (Fig. 8). This shows that the plant is enriched in Mn, Cd, Al, Cu, Pb, and Fe at this site. Since As was not found in the sample taken from the uncontaminated site, the EF^{Plant} value for As could not be calculated. However, since the average As value was calculated as 4.79 mg/kg in the samples taken from the contaminated site, it is believed that there is As accumulation in the Scotch pine tree. The ratio between plant and soil concentrations (BCF) is an index of the soil-to-plant transfer of an element, which helps to understand the plant uptake characteristics. BCF values between 1 and 10 indicate that plants accumulate these elements, while BCF values greater than 10 indicate that the plant is an accumulator (Jonczak et al. 2021). In the samples taken from the scotch pine needles around the abandoned mine, BCF values were as follows: Mn (5.76) > Zn (0.25) > Al (0.08) > Cd (0.06) > Cr (0.04) > Cu (0.01) > Pb (0.01) > As (0.01). We can conclude that while the Scotch pine tree appears to accumulate Mn, accumulation was not very significant for other PTEs.

Statistical evaluation

Variation in the levels of metal and metalloids in the soil and plants across different regions was analyzed using the non-parametric Kruskal-Wallis H -test and Spearman-Brown correlations, due to the non-homogeneous distribution of the data (Table 5). The findings indicate that all metal concentrations in the soil samples show statistically significant variability across sample regions ($p < 0.05$). Furthermore, the concentrations of As, Pb, Cd, Fe, and Cu generally followed the order of Regions 1 > 2 > 3 > 4 > 5. However, the lowest concentrations of Mn and Al were obtained from the samples in Region 1. This could be explained by the rapid transformation of the metal released from samples into a soluble form due to acidic conditions and seasonal rainfall, specifically for Mn and Al (Doğrul Demiray 2017).

When the Kruskal-Wallis results of the plant samples were statistically evaluated, it was determined that the amounts of As, Pb, and Cd varied significantly across regions ($p < 0.05$), and the highest concentrations were found in plants in Region 2. Additionally, it was found that the concentrations of Fe and Al, which are among the measured metal groups, showed similar characteristics in Regions 2, 3, and 4, but had higher concentrations than the control regions ($p < 0.05$). The results of the Spearman-Brown correlations for the soil samples are shown in Table 5.

The data revealed a strong positive correlation between AS and pH ($r = 0.772$, $p < 0.01$), and a moderate-strong correlation was found between AS and total lime ($r = 0.570$, $p < 0.01$). In addition, in the correlation analysis among metals, a strong positive correlation was found between As and Pb ($r = 0.96$, $p < 0.01$) and between As and Cd ($r = 0.97$, $p < 0.01$), while moderate-strong correlations were observed between As and Fe ($r = 0.69$, $p < 0.01$), As and Cu ($r = 0.60$, $p < 0.01$), and between Al and Mn ($r = 0.57$, $p < 0.01$).

When all the data from the study is evaluated, it is important to identify the distribution and environmental impacts

Fig. 8 Metal and metalloids enrichment factor of plant (EF^{Plant}) of Kuvarshan mine area

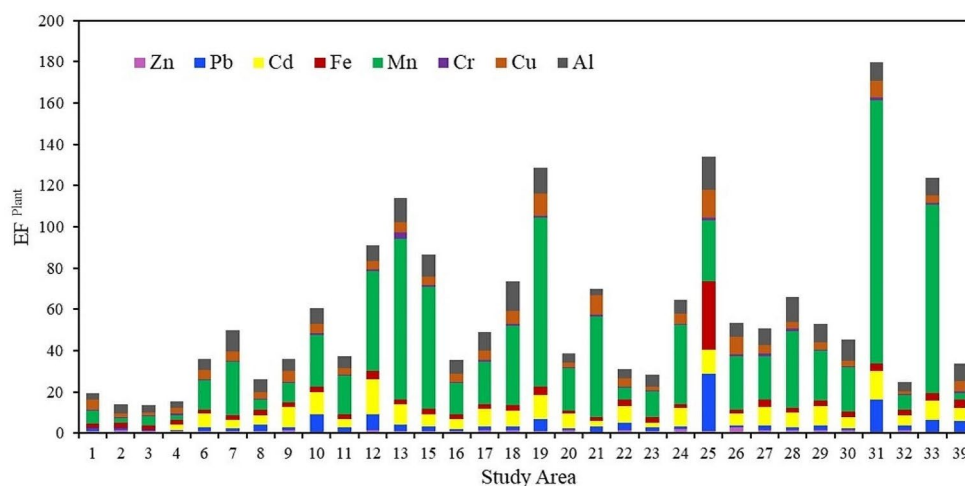


Table 5 Correlation findings

	(%)AS	(%)Sand	(%)Clay	(%)Silt	(%)CaCO ₃	pH	Conductivity	As	Zn	Pb	Cd	Ni	Fe	Mn	Cr	Cu
(%)Sand	0.256															
(%)Clay	0.217	-0.354*														
(%)Silt	-0.358*	-0.800**	-0.174													
(%)CaCO ₃	0.570**	0.014	0.198	-0.129												
pH	0.772**	0.141	0.232	-0.236	0.689**											
Conductivity	-0.610**	-0.314*	-0.327*	0.452**	-0.440**	-0.662**										
As	-0.606**	-0.165	-0.091	0.228	-0.562**	-0.739**	0.570**									
Zn	-0.326*	0.168	-0.158	-0.025	-0.216	-0.279	0.218	0.515**								
Pb	-0.566**	-0.100	-0.126	0.195	-0.553**	-0.737**	0.573**	0.962**	0.542**							
Cd	-0.589**	-0.144	-0.076	0.215	-0.534**	-0.672**	0.508**	0.978**	0.571**	0.944**						
Ni	0.768**	0.133	0.111	-0.187	0.688**	0.897**	-0.588**	-0.761**	-0.310*	-0.778**	-0.706**					
Fe	-0.660**	0.122	-0.378*	0.088	-0.547**	-0.708**	0.578**	0.694**	0.621**	0.699**	0.668**	-0.680**				
Mn	0.722**	0.274	0.113	-0.230	0.545**	0.841**	-0.587**	-0.708**	-0.117	-0.672**	-0.642**	0.843**	-0.594**			
Cr	0.214	0.252	-0.078	-0.251	0.230	0.274	-0.187	-0.076	-0.018	-0.095	-0.041	0.447**	-0.050	0.213		
Cu	-0.418**	0.192	-0.296	0.019	-0.383*	-0.351*	0.303	0.599**	0.827**	0.600**	0.654**	-0.345*	0.683**	-0.195	0.165	
Al	0.426**	0.020	-0.019	0.041	0.192	0.476**	-0.362*	-0.367*	0.017	-0.307	-0.299	0.423**	-0.356*	0.578**	-0.152	-0.136

** $p < 0.01$ * $p < 0.05$

of the primary pollutant metal groups, similar to many abandoned copper mining sites. In this context, the data obtained from many field studies reveal that As, Pb, Cu, Cd, and Fe elements are regularly found to be potential pollutants. The spread of these pollutants from waste sites can be determined by evaluating factors such as geological structure and vegetation in combination.

Previous studies of the geological structure of the area reveal that geological formations consist of chalcopyrite, bornite, neodymium, chalcocite, sphalerite, and secondary-level galena and tetrahedrite, and that the Kuvarshan region has a tenor of 2.16% Cu and 47.4% S (Kovenko 1942; MTA 2010). Previous studies have shown that the ore-bearing dacite and waste rock piles located in the waste site area contribute significantly to the development of acid and metal drainage, as evidenced by static and kinetic tests (Doğrul Demiray 2017).

Conclusion

The aim of this research was to evaluate metal and metalloids contamination in soil and plant samples from an abandoned copper mining site in Kuvarshan. The contamination and ecological impacts of metals and metalloids found in soil and plant samples in and around the abandoned copper mining site in Kuvarshan region were evaluated. The findings show the environmental impacts of mining activities and the potential risks to human health.

- High levels of As, Cd, Cu, Pb and Zn pollution were detected in EF and Igeo indexes in soil samples. This contamination is mainly due to copper mining activities.
- In plant samples, high levels of metal and metalloids accumulation were observed in Scotch pine needles, especially Mn, Al, Fe, Zn and Cu.
- In areas where metal and metalloids accumulation is high in plants and soil, ecological risk can pose a serious threat to ecosystems and human health.
- Human health risk assessment indicates that high levels of As, Pb and other metal and metalloids may pose a potential carcinogenic risk.
- Contamination and deposition in soil and plant samples in and around the mine site indicate the long-term environmental impacts of former mining activities and the potential for contamination to spread.

In conclusion, this study reveals the environmental impacts and potential risks of abandoned mine sites. In future research, it is important to focus on rehabilitating these abandoned sites. Serious studies should be conducted on measures to reduce soil pollution. Factors such as the

proximity of the site to underground and surface resources in the vicinity of the site and prevailing wind directions should be determined, and airborne transport should be modeled. In this direction, it is recommended that artificial intelligence-based pollution model predictions be made in the following stages. These studies will be an important step to minimize the environmental impacts of abandoned mine sites and increase environmental sustainability.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s12665-024-11725-9>.

Author contributions MUK and GDD wrote the main manuscript. MUK participated in the field investigation Sampling. İAK participated in validation. İAK and EY participated in statistical analysis evaluation. The published version of the work has been reviewed and approved by all authors.

Funding This work wasn't supported by institutional funds. Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK).

Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Competing interests The authors declare that they have no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Bayraklı B, Dengiz O, Özyazıcı MA et al (2023) Assessment of heavy metal concentrations and behavior in cultivated soils under humid-subhumid environmental condition of the Black Sea region. *Geoderma Reg* 32:e00593. <https://doi.org/10.1016/j.geoder.2022.e00593>
- Beane SJ, Comber SDW, Rieuwerts J, Long P (2016) Abandoned metal mines and their impact on receiving waters: a case study from Southwest England. *Chemosphere* 153:294–306. <https://doi.org/10.1016/j.chemosphere.2016.03.022>
- Bierza W, Bierza K, Trzebny A et al (2020) The communities of ectomycorrhizal fungal species associated with *Betula pendula*

- Roth and *Pinus sylvestris* L. growing in heavy-metal contaminated soils. *Plant Soil* 457:321–338. <https://doi.org/10.1007/s11104-020-04737-4>
- Carvalho MEA, Gaziola SA, Carvalho LA, Azevedo RA (2021) Cadmium effects on plant reproductive organs: physiological, productive, evolutionary and ecological aspects. *Ann Appl Biol* 178:227–224. <https://doi.org/10.1111/aab.12612>
- Chen J, He F, Zhang X et al (2014) Heavy metal pollution decreases microbial abundance, diversity and activity within particle-size fractions of a paddy soil. *FEMS Microbiol Ecol* 87(1):164–181. <https://doi.org/10.1111/1574-6941.12212>
- Chen L, Zhou M, Wang J et al (2022) A global meta-analysis of heavy metal(loid)s pollution in soils near copper mines: evaluation of pollution level and probabilistic health risks. *Sci Total Environ* 835:155441. <https://doi.org/10.1016/j.scitotenv.2022.155441>
- Cheng Y, Zhou K, Wang J et al (2022) Regional metal pollution risk assessment based on a big data framework: a case study of the eastern Tianshan mining area, China. *Ecol Indic* 145:109585. <https://doi.org/10.1016/j.ecolind.2022.109585>
- Chileshe MN, Syampungani S, Festin ES et al (2020) Physico-chemical characteristics and heavy metal concentrations of copper mine wastes in Zambia: implications for pollution risk and restoration. *J Res* 31:1283–1293. <https://doi.org/10.1007/s11676-019-00921-0>
- Çomaklı E, Bingöl MS (2021) Heavy metal accumulation of urban scots pine (*Pinus sylvestris* L.) plantation. *Environ Monit Assess* 193:192. <https://doi.org/10.1007/s10661-021-08921-6>
- Covre WP, Ramos SJ, Pereira WV da S, et al (2022) Impact of copper mining wastes in the Amazon: Properties and risks to environment and human health. *J Hazard Mater* 421:126688. <https://doi.org/10.1016/j.jhazmat.2021.126688>
- CSB (2010) Toprak kirliliğinin kontrolü ve noktasal kaynaklı kirlenmiş sahalara dair yönetmelik. <https://www.resmigazete.gov.tr/eskiler/2010/06/20100608-3.htm>. Accessed 24 Nov 2023
- Dary M, Chamber-Pérez MA, Palomares AJ, Pajuelo E (2010) In situ phytostabilisation of heavy metal polluted soils using *Lupinus luteus* inoculated with metal resistant plant-growth promoting rhizobacteria. *J Hazard Mater* 177:323–330. <https://doi.org/10.1016/j.jhazmat.2009.12.035>
- Flores de la Torre JA, Mitchell K, Ramos Gómez MS et al (2018) Effect of plant growth on pb and zn geoaccumulation in 300-year-old mine tailings of Zacatecas, México. *Environ Earth Sci* 77:1–9. <https://doi.org/10.1007/s12665-018-7563-7>
- Dogangün Yasa B, Yardımcı ME (2022) Development of copper mining in the light of Statistic politics of Economy: the case of Etibank (1935–1950). *J Hist Sch* 57:1407–1433. <https://doi.org/10.29228/joh.54984>
- Doğrul Demiray A (2017) Geochemical processes controlling the generation and environmental impacts of acid mine drainage in the case of polymetallic mines, Artvin. Dissertation, Kocaeli University
- Element CAS (2007) Method 3051A microwave assisted acid digestion of sediments, sludges, soils, and oils. *Z Für Anal Chem* 111:362–366
- Fernández-Caliani JC, Barba-Brioso C, González I, Galán E (2009) Heavy metal pollution in soils around the abandoned mine sites of the iberian pyrite belt (Southwest Spain). *Water Air Soil Pollut* 200:211–226. <https://doi.org/10.1007/s11270-008-9905-7>
- Ferreira SLC, da Silva Junior JB, dos Santos IF et al (2022) Use of pollution indices and ecological risk in the assessment of contamination from chemical elements in soils and sediments – practical aspects. *Trends Environ Anal Chem* 35:e00169. <https://doi.org/10.1016/j.teac.2022.e00169>
- Gök N (2008) The documents which relate to Artvin Liva after it came under the Turkish control. *Atatürk Yolu Dergisi* 11(41):89–104. https://doi.org/10.1501/Tite_0000000254
- Golia EE (2023) The impact of heavy metal contamination on soil quality and plant nutrition. Sustainable management of moderate contaminated agricultural and urban soils, using low cost materials and promoting circular economy. *Sustain Chem Pharm* 33:101046. <https://doi.org/10.1016/j.scp.2023.101046>
- Hadjipanagiotou C, Christou A, Zissimos AM et al (2020) Contamination of stream waters, sediments, and agricultural soil in the surroundings of an abandoned copper mine by potentially toxic elements and associated environmental and potential human health-derived risks: a case study from Agrokipia, Cyprus. *Environ Sci Pollut Res* 27:41279–41298. <https://doi.org/10.1007/s11356-020-10098-3>
- Hakanson L (1980) An ecological risk index for aquatic pollution control: a sedimentological approach. *Water Res* 14:975–1001. [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)
- Horasan BY, Ozturk A, Tugay O (2021) Nb–Sr–Pb isotope analysis in soils of abandoned mercury quarry in northwest Black Sea (Turkey), soil and plant geochemistry, evaluation of ecological risk and its impact on human health. *Environ Earth Sci* 80:488. <https://doi.org/10.1007/s12665-021-09775-4>
- Jonczak J, Sut-Lohmann M, Polláková N et al (2021) Bioaccumulation of potentially toxic elements by the Needles of Eleven Pine Species in Low Polluted Area. *Water Air Soil Pollut* 232:28. <https://doi.org/10.1007/s11270-020-04959-3>
- Kabata-Pendias A (2004) Soil-plant transfer of trace elements—an environmental issue. *Geoderma* 122(2–4):143–149. <https://doi.org/10.1016/j.geoderma.2004.01.004>
- Karczewska A, Mocek A, Goliński P, Mleczyk M (2015) Phytoremediation of copper- contaminated soil. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) *Phytoremediation*. Springer, pp 143–170. https://doi.org/10.1007/978-3-319-10969-5_12
- Khafouri A, Talbi EH, Abdelouas A (2021) Assessment of Heavy Metal Contamination of the Environment in the mining site of Ouixane (North East Morocco). *Water Air Soil Pollut* 232:398. <https://doi.org/10.1007/s11270-021-05318-6>
- Khalil A, Taha Y, Benzaazoua M et al (2023) Applied methodological approach for the assessment of soil contamination by trace elements around abandoned coal mines—A case study of the Jerada coal mine, Morocco. *Minerals* 13(2):181. <https://doi.org/10.3390/min13020181>
- Khan ZI, Ugulu I, Zafar A et al (2021) Biomonitoring of heavy metals accumulation in wild plants growing at soon valley, Khushab, Pakistan. *Pakistan J Bot* 53:247–252. [https://doi.org/10.30848/PJB2021-1\(14\)](https://doi.org/10.30848/PJB2021-1(14))
- Khan J, Singh R, Upreti P et al (2022) Geo-statistical assessment of soil quality and identification of heavy metal contamination using Integrated GIS and multivariate statistical analysis in Industrial region of Western India. *Environ Technol Inno* 28:102646. <https://doi.org/10.1016/j.eti.2022.102646>
- Klink A, Polechońska L, Dambiec M, Białas K (2018) A comparative study on macro- and microelement Bioaccumulation properties of leaves and Bark of *Quercus petraea* and *Pinus sylvestris*. *Arch Environ Contam Toxicol* 74:71–79. <https://doi.org/10.1007/s00244-017-0439-0>
- Konanc MU (2021) Evaluation of Olive Tree (*Olea europaea* L.) as a Biomonitor for Monitoring of Heavy Metal Pollution caused by traffic: Example of Artvin. *J Nat Hazards Environ* 7:13–26. <https://doi.org/10.21324/dacd.766802>
- Kovenko V (1942) Mines De cuivre de kuvarshan de la region d'Artvin. *MTA Mecm* 2:230–266
- Loska K, Wiechulla D, Korus I (2004) Metal contamination of farming soils affected by industry. *Environ Int* 30:159–165. [https://doi.org/10.1016/S0160-4120\(03\)00157-0](https://doi.org/10.1016/S0160-4120(03)00157-0)
- Madejón P, Maraño T, Murillo JM (2006) Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak

- trees. *Sci Total Environ* 355:187–203. <https://doi.org/10.1016/j.scitotenv.2005.02.028>
- Masson P, Prunet T, Orignac D (2006) Arsenic determination in plant samples by hydride generation and axial view inductively coupled plasma atomic emission spectrometry. *Microchim Acta* 154:229–234. <https://doi.org/10.1007/s00604-006-0516-y>
- Men C, Liu R, Xu F et al (2018) Pollution characteristics, risk assessment, and source apportionment of heavy metals in road dust in Beijing, China. *Sci Total Environ* 612:138–147. <https://doi.org/10.1016/j.scitotenv.2017.08.123>
- Motswaiso F, Nakamura K, Watanabe N et al (2019) Geochemical Investigation of Metals and Trace Elements around the abandoned Cu-Ni mine site in Selibe Phikwe, Botswana. *J Geosci Environ Prot* 7(5):275–293. <https://doi.org/10.4236/gep.2019.75020>
- MTA (2010) Artvin ili maden ve enerji kaynakları. <https://www.mta.gov.tr/v3.0/bilgi-merkezi/il-maden-potansiyelleri>. Accessed 24 Nov 2023
- Pajak M, Gąsiorek M, Cygan A, Wanic T (2015) Concentrations of cd, pb and zn in the top layer of soil and needles of scots pine (*Pinus sylvestris* L.): a case study of two extremely different conditions of the forest environment in Poland. *Fresenius Environ Bull* 24:71–76
- Parzych A, Jonczak J (2014) Pine needles (*Pinus sylvestris* L.) as bioindicators in the assessment of urban environmental contamination with heavy metals. *J Ecol Eng* 15:29–38. <https://doi.org/10.12911/22998993.1109119>
- Parzych A, Mochacký S, Sobisz Z et al (2017) Accumulation of heavy metals in needles and bark of *Pinus* species. *Folia Pol Ser A* 59:34–44. <https://doi.org/10.1515/fp-2017-0004>
- Paternie EDE, Hakkou R, Nga LE et al (2023) Geochemistry and geostatistics for the assessment of trace elements contamination in soil and stream sediments in abandoned artisanal small-scale gold mining (Bétaré-Oya, Cameroon). *Appl Geochem* 150:105592. <https://doi.org/10.1016/j.apgeochem.2023.105592>
- Pehlivan N, Gedik K, Eltem R, Terzi E (2021) Dynamic interactions of *Trichoderma Harzianum* TS 143 from an old mining site in Turkey for potent metal(oid)s phytoextraction and bioenergy crop farming. *J Hazard Mater* 403:123609. <https://doi.org/10.1016/j.jhazmat.2020.123609>
- Punia A (2021) Role of temperature, wind, and precipitation in heavy metal contamination at copper mines: a review. *Environ Sci Pollut Res* 28:4056–4072. <https://doi.org/10.1007/s11356-020-11580-8>
- Quintero-Payan AC, Huete-Hernández S, Aguilar-Pozo VB et al (2024) Stabilization of metal and metalloids from contaminated soils using magnesia-based tundish desludging waste from continuous steel casting. *Chemosphere* 348:140750. <https://doi.org/10.1016/j.chemosphere.2023.140750>
- Shabanda IS, Koki IB, Raof SFA et al (2021) Distribution of heavy metals in roadside dust of Petaling Jaya, Malaysia with multivariate and correlation analyses for source identification. *Int J Environ Anal Chem* 101:184–207. <https://doi.org/10.1080/03067319.2019.1661400>
- Shen Q, Wu M, Zhang M (2022) Accumulation and relationship of metals in different soil aggregate fractions along soil profiles. *J Environ Sci* 115:47–54. <https://doi.org/10.1016/j.jes.2021.07.007>
- Sousa NR, Ramos MA, Marques APGC, Castro PML (2012) The effect of ectomycorrhizal fungi forming symbiosis with *Pinus pinaster* seedlings exposed to cadmium. *Sci Total Environ* 414:63–67. <https://doi.org/10.1016/j.scitotenv.2011.10.053>
- Srinivasa Gowd S, Ramakrishna Reddy M, Govil PK (2010) Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *J Hazard Mater* 174:113–121. <https://doi.org/10.1016/j.jhazmat.2009.09.024>
- Steingraber LF, Ludolph C, Metz J et al (2022) Uptake of lead and zinc from soil by blackberry plants (*Rubus fruticosus* L. Agg.) And translocation from roots to leaves. *Environ Adv* 9:100313. <https://doi.org/10.1016/j.envadv.2022.100313>
- Thompson M, Ellison SLR, Wood R (2002) Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC Technical Report). *Pure Appl Chem* 74:835–855. <https://doi.org/10.1351/pac200274050835>
- Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen* 33:566–575. <https://doi.org/10.1007/BF02414780>
- Tuğba Ş, Kalkancı N, Büyük G (2021) Determination of heavy metal pollution levels in agricultural soils: the case of Osmaniye. *Mustafa Kemal Univ J Agric Sci* 26:106–116. <https://doi.org/10.37908/mkutbd.804262>
- Verdejo J, Ginocchio R, Sauvé S et al (2015) Thresholds of copper phytotoxicity in field-collected agricultural soils exposed to copper mining activities in Chile. *Ecotoxicol Environ Saf* 122:171–177. <https://doi.org/10.1016/j.ecoenv.2015.07.026>
- Xiao X, Zhang J, Wang H et al (2020) Distribution and health risk assessment of potentially toxic elements in soils around coal industrial areas: a global meta-analysis. *Sci Total Environ* 713:135292. <https://doi.org/10.1016/j.scitotenv.2019.135292>
- Yakupoglu T, Şişman AÖ, Gündoğan R (2015) Predicting of Soil Aggregate Stability values using Artificial neural networks. *Turkish J Agric Res* 2(2):83–92. <https://doi.org/10.19159/tutad.40383>
- Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China - Weathering features, anthropogenic impact and chemical fluxes. *Estuar Coast Shelf Sci* 54:1051–1070. <https://doi.org/10.1006/ecss.2001.0879>
- Zhen Q, Zheng J, Zhang X, Shao M (2019) Changes of solute transport characteristics in soil profile after mining at an opencast coal mine site on the Loess Plateau, China. *Sci Total Environ* 665:142–152. <https://doi.org/10.1016/j.scitotenv.2019.02.035>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.