



# Environmental effects of acid mine drainage and rehabilitation options at closed mine site: a case study

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**Abstract** Irregular waste storage at closed mine sites poses severe environmental problems. This study evaluates the concentrations and effects of trace elements released into the environment by mining activity by analyzing soil, water, and sediment samples taken from a copper mining site. According to the data, acidic mine drainage was the main cause of the high concentrations of trace elements in the soil and sediments, including arsenic (As), cadmium (Cd), lead (Pb), and copper (Cu). The concentrations of As, Cd, Pb, and Cu in soil and sediments were 2734-times, 1189-times, 157-times and 32 times higher, respectively, in comparison to the background values of averaged concentrations of these elements in the upper crust. Geological and statistical studies

indicate that the primary constituents of these pollutants are chalcopyrite and pyrite derivatives present in the primary rock structure. Using water analysis data from 2011 to 2020, the release of essential trace element into water was investigated to monitor the environmental effects of acidic mine drainage (AMD) from the closed Kuvarshan copper mine in the Artvin region of Turkey. This study demonstrates that trace elements concentrations may change according to local and seasonal factors and highlights the importance of conducting routine environmental monitoring studies.

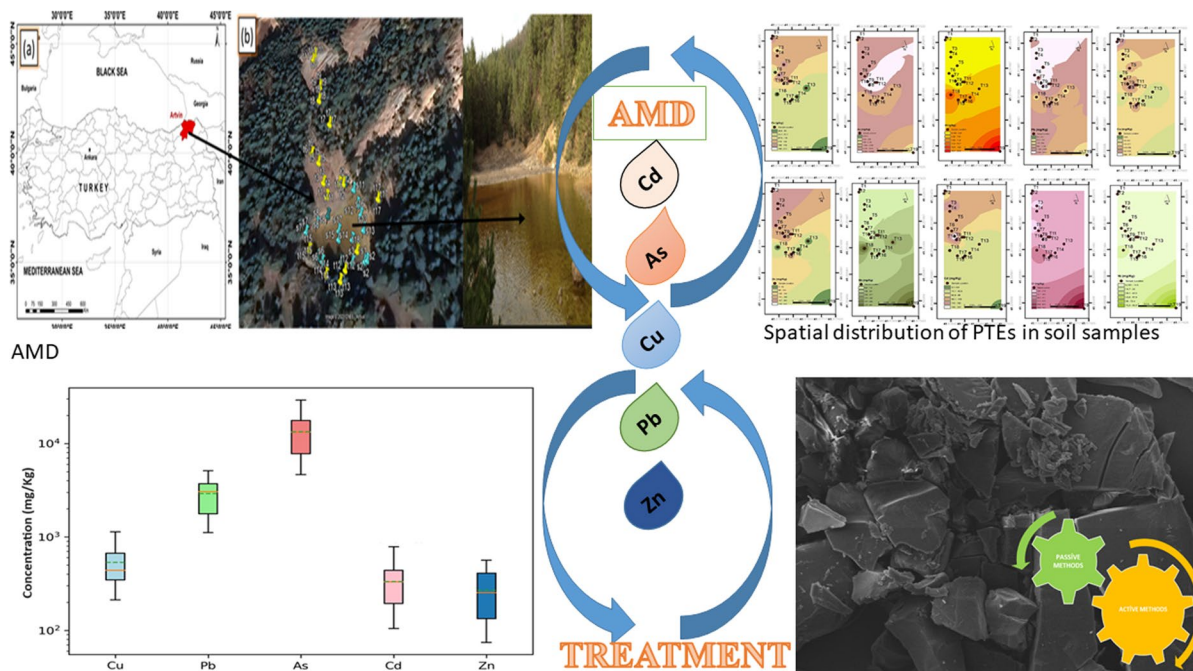
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## Graphical Abstract



**Keywords** Environmental monitoring · Abandoned mine · Trace elements pollution · Acidic mine drainage

## Introduction

Mining supplies most of modern society's basic industrial raw materials. Copper mining is critical for the transition to fossil-free energy required to achieve sustainable development worldwide and plays a crucial role in modern society (Texeira et al., 2023). However, mining activities can potentially lead to various problems. These problems include the destruction of land, water pollution, acid mine drainage (AMD), air pollution (through the release of gas and dust), noise pollution, mine fires, damage to forest flora and fauna, and health risks (Vasquez Ugaz et al., 2023). AMD in particular is a severe worldwide environmental problem that can significantly affect natural water resources (Zheng et al., 2023). In mining areas, sulphur-containing minerals (mainly pyrite and other sulphide ores) are formed

due to the ores with air, water or microorganisms. When sulphides come into contact with oxygen and water, the formation of sulfuric acid takes place as a natural process leading to the precipitation of dissolved iron, which is first oxidized from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and then precipitated by hydrolysis as ferric oxyhydroxide (Kaur et al., 2018). The materials spread into the environment by AMD have low pH, high salinity and hardness, strong solubility and corrosiveness, and their acidic chemistry is extremely unstable, often affected by seasonal and daily changes (Jiao et al., 2023). The acid ( $\text{H}^+$ ) formed during the oxidation of sulphurous minerals can cause the dissolution of other mineralogical phases containing potentially toxic elements such as Cu, Zn, Pb, As, Cd, and Fe (Ruiz-Sánchez et al., 2023). These acidic solutions can pollute natural ecosystems and agricultural areas close to mines, especially the surface and groundwater, and these pollutants can be carried to distant places where they can lead to even greater dangers (Ding et al., 2021). Severe rainstorms at mining sites lead to the release of large amounts of contaminated water

which can directly transport trace elements into ecosystems, severely impacting local vegetation or causing extreme metal stress in crops (Hajihashemi et al., 2023). Among the most serious water pollutions worldwide, AMD is ranked “second only to global warming and ozone depletion” by the USA Environmental Protection Agency (US-EPA) in terms of ecological risk (Moodley et al., 2018).

In the literature on the environmental pollution levels of closed mine sites, it has been observed that AMD leaks originating from the abandoned Tharsis mine located in the Iberian Pyrite Belt place a high burden on watercourses (Moreno-González et al., 2022). Additionally, a study has found that trace elements and other harmful materials transported by AMD at an abandoned mine site in southwestern China were released into surrounding waters, posing a direct threat to the health of local people (Zhu et al., 2022). High concentrations of harmful materials have also been detected in fluvial sediments and surface debris originating from an abandoned mine site at Lakhouat in northern Tunisia (Ayari et al., 2023).

This study aimed to estimate the amount of these metals based on the hypothesis that although the Kuvvarshan copper mine in Artvin region was closed about 75 years ago, the tailings piles are subject to decomposition and continuously release trace elements into the environment. To this end, soil, water, and sediment samples were collected to measure the amount of trace elements originating from waste in the closed mining area, and their concentrations were determined. The potential effects of trace elements found in significant concentrations in soil and

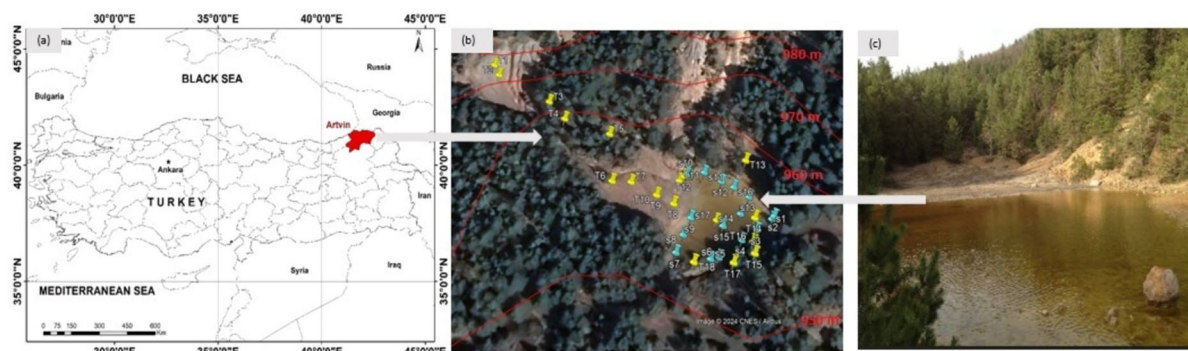
sediments were then evaluated both geochemically and environmentally.

## Materials and methods

### Sampling

Kuvvarshan (41° 14.746 N; 41° 49.283 D) is a closed mine site in the Eastern Black Sea region of Turkey that was in operation from 1905 to 1945 (Fig. 1). The mine was initially operated by B. Siemens under the Caucasus Copper Limited between 1905 and 1928. The Turkish copper mines were handed over to Eti-bank Copper Works, which was established in 1936. During the period 1937–1941 8,800 tons of metallic copper was produced in the Kuvvarshan copper mine. At this time is closed. The mine has two types of mineralisation as described by Wijkerslooth (1946). The upper part consists of a copper-poor pyrite zone (Gelberze), while the lower part contains a copper-rich zone (Grauzere). The copper-poor pyrite zone consists of pyrite, chalcopyrite and accessory galena, with copper assays ranging from 1 to 1.5% Cu. The lower copper-rich zone consists of chalcopyrite, bornite, chalcocite and tennantite, with copper assays of 6–7% Cu. (Wijkerslooth (1946), Kraeff., 1963)

The mine site is located in a large area that includes a smelter and several former mine galleries that are now closed. So, a total of 18 soil were collected using a random sampling model in different numbers in September 2020 from five different sample points in the mining area; 17 water, 17 sediment and control samples were collected (Suppl. Table 1). The soil and sediment samples collected at each site



**Fig. 1** a Location map of the study area b the sampling sites and c acid pond formed in the mine waste

consisted of 4–5 composite samples collected at a depth of 0–10 cm from the surface of the mining area. After sampling, the soil, sediments and water samples were sealed in clean polyethylene bags or polyethylene cups, placed in a refrigerator at 4 °C, and immediately transported for analysis to minimize the effects of environmental conditions. Different analytical procedures were applied for group of samples, which were classified into three different categories. Both the soil and sediment samples were kept in an air-dry environment for a week. Then, the soil and sediment samples were homogenized by passing them through a 2 mm sieve to remove plant residue, stones, and other residues. All homogenized soil and sediment samples were transferred to polyethylene bags and prepared for physicochemical tests. The water samples from the acidic pond that had formed in the mine waste were filtered through 0.45 µm filters, transferred to amber bottles to avoid interference from light, and stored at 4 °C until analysis.

#### Physicochemical analyses

The pH and conductivity values of the soil and sediment samples were measured using a Hach Lange Multimeter (HQ40D) at a 1/5 ratio of solids to water. Total lime percentage was determined using n; a Schibber calcimeter. Classification of the samples based on particle size was done using the Bouyoucus hydrometer method. Finally, the texture of the samples was determined by the percentage of sand, silt and clay on United States Department of Agriculture (USDA) texture triangle NRSC (Natural Resources Conservation Service, 2013). For physicochemical analysis of the water samples, pH, conductivity, total dissolved solids (TDS), and salinity values were measured directly via a Hach Lange multimeter. Total sulfate ( $\text{SO}_4^{2-}$ ) values were determined using a Shimadzu UV-1800 spectrophotometer. Total  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  were determined using a flame spectrophotometer (BWB XP Flame Photometer).

The SEM-EDS analysis was carried out to provide preliminary information on the primary material and trace elements present in the soil. Subsequently; trace element concentrations in the soil, sediment and water samples were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-OES; Perkin Elmer Optima 8000) after microwave digestion (Suppl. Table 2, Suppl. Figure 1). After digestion

process, 1 mg/L of internal standard (yttrium) was added to all samples and the final volume of each sample was completed to 50 mL. Trace element concentrations (Cu, Zn, Pb, As, Cr, Cd, Ni, Mn, Al and Fe) were analysed in all samples by ICP-OES.

#### Analytical procedure

Reagent blanks, replicates and certified standard reference materials (Sigma-CRM 027 Sandy Loam 10; LGC 6187 River Sediment and LGC SPS-SW2 Batch 135 Surface Water) for the three different categories (soil, sediment and water) of samples were included in the analysis to determine the accuracy and precision of the measurements used in the analytical procedure and to evaluate the sensitivity and bias of the method. According to the analytical results, the precision and bias of the method were generally <5%. Recovery rates were consistent with certified concentrations. Additionally, LOD and LOQ were calculated together with their standard deviations (SD) for each analyte. The Limit of Detection was calculated as  $(\text{LOD}) = \text{LOQ} = \text{mean}_{\text{blank}} + 3\text{SD}_{\text{blank}}$ , and the lowest concentration that could be determined with an acceptable precision, was calculated as  $(\text{LOQ}) = \text{LOQ} = \text{mean}_{\text{blank}} + 10\text{SD}_{\text{blank}}$ . These values determined using the coefficient (IUPAC, 1978).

#### Statistical analysis

SPSS version 19 was used to monitor the trace element pollution resulting from abandoned mine tailings and analyse possible potential risk factors. Principal component analysis (PCA) was used to determine the potential sources or origins of each analyte in the soil, water and sediment samples taken from the sampling site. Additionally, Pearson correlation coefficients were used to determine the relationship between trace elements and physicochemical analyses.

#### Soil and sediment pollution index evaluation

Geo-accumulation indices ( $I_{\text{geo}}$ ) and contamination factors (CF) were calculated to evaluate the trace elements (As, Zn, Pb, Cd, Ni, Fe, Mn, Cr, Cu and Al) pollution measured by means of the analysis of soil and sediment samples taken from the AMD site (Suppl. Table 8). The geo-accumulation index

( $I_{\text{geo}}$ ) was proposed by Müller in 1969 as a way to evaluate pollution levels in bottom sediments. Later, it used to calculate soil pollution (Ferreira et al., 2022). The values suggested by Wedepohl (1995) for the average metal concentrations in the upper crust of the Earth (Supp. Table 9) were used in this study (Wedepohl, 1995, ). By comparing the concentrations of trace elements measured in the soil with these geochemical background values (Barkett & Akün, 2018), we can calculate whether these pollutants are of natural or anthropogenic origin. These background values are widely used in the evaluation of trace elements pollution in soil, which was calculated in this study using the equation below (Eq. 1) (Müller, 1969).

$$I_{\text{geo}} = \log_2 \left[ \frac{C_s}{1.5 \times B_n} \right] \quad (1)$$

where  $C_s$  is the concentration of a given trace elements as measured in the soil sample ( $\text{mg kg}^{-1}$ ), and  $B_n$  is geochemical background value of the given trace elements ( $\text{mg kg}^{-1}$ ). The coefficient of 1.5 minimizes the effect of possible changes in background values (Li et al., 2012). With respect to geo-accumulation ( $I_{\text{geo}}$ ) values, if  $I_{\text{geo}} \leq 0$ , there is no contamination, if  $0 \leq I_{\text{geo}} \leq 1$  then there is no contamination to moderate contamination, if  $1 \leq I_{\text{geo}} \leq 2$  then there is moderate contamination, if  $2 \leq I_{\text{geo}} \leq 3$  then there is moderate to severe contamination, if  $3 \leq I_{\text{geo}} \leq 4$  then there is severe contamination, if  $4 \leq I_{\text{geo}} \leq 5$  then there is severe to very severe contamination, and if  $5 < I_{\text{geo}}$  then there is extremely high contamination.

The contamination factor (CF) is crucial for determining the degree of pollution. CF is calculated using the following equation (Eq. 2) (Hakanson, 1980).

$$CF = \frac{C_s}{C_{\text{ref}s}} \quad (2)$$

where  $C_s$  is the concentration of a given element as measured in the soil sample ( $\text{mg kg}^{-1}$ ), and  $C_{\text{ref}s}$  is the concentration of a given element in the reference soil ( $\text{mg kg}^{-1}$ ). With respect to CF values: if  $CF \leq 1$  then there is low contamination, if  $1 \leq CF \leq 3$  then there is moderate contamination, if  $3 \leq CF \leq 6$  then there is significant contamination, and if  $6 \leq CF$  then there is very high contamination.

## Results and discussion

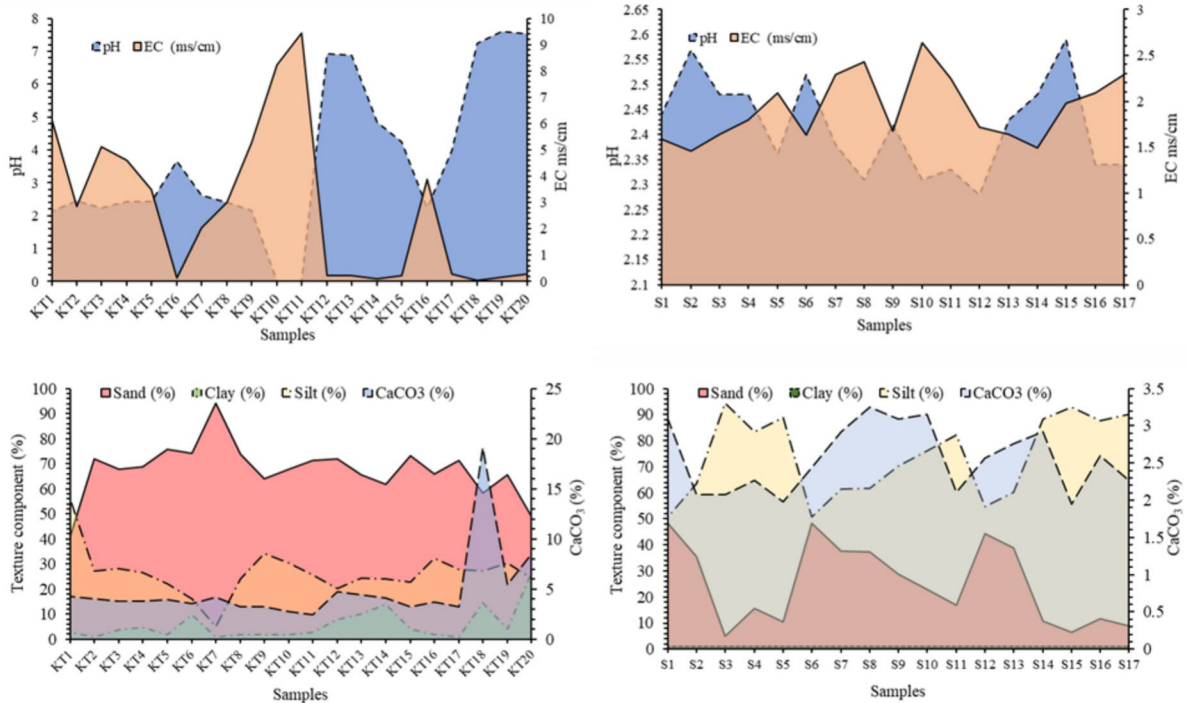
### Evaluation of geological structure and physicochemical analysis

The pH of soil, sediment, and water samples taken from the Kuvashan AMD site varied between  $< 1$ –7.61, 2.28–2.59 and 2.02–6.82, respectively. The measured conductivity values for the soil, s ediment, and water samples ranged from 0.053 to 9.45  $\text{mS cm}^{-1}$ , 1.46 to 2.64  $\text{mS cm}^{-1}$  and 0.1049 to 4.19  $\text{mS cm}^{-1}$ , respectively. The equivalent calcium carbonate contents of the soil and sediment samples taken in the field ranged from 2.44 to 19.11%, and from 1.95 to 3.25%, respectively. When the textural characteristics of the soil and sediment samples were examined, the soil samples were generally found to be sandy silt in nature, while the sediment samples were found to be dusty loam (Fig. 2).

According to Fig. 2, the lowest pH ( $< 1.0$ ) and highest conductivity (9450  $\mu\text{S/cm}$ ) values were detected in the soil samples taken from the KT11 sample point, where the mine tailings are located. In the textural structure of the soil samples taken from the field, the average sand fraction was dominant at 66.42%, the silt content was moderate at 25.45%, and the clay content was 5.61%. In areas with this type of textural structure, the low pH and high conductivity values obtained from experimental data confirm that the transport of trace elements to other points is influenced by land slope, climatic changes, and geological structure.

The soil and water samples collected from the mining area exhibited acidic characteristics. This acidity is a crucial factor influencing the behavior of potentially toxic elements (PTEs) in mining environments, particularly their presence, persistence, and mobility. In areas of copper (Cu) mining, low pH values are common due to the abundance of sulfide minerals, which release PTEs under oxidizing conditions (Covre et al., 2022; Konanç et al. 2024).

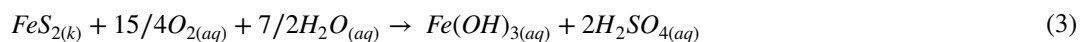
The textural structure of the sediment samples accumulated from the AMD site indicates that the average particle size was silty, with 72.63% of the upper fractions consisting of silt; this finding is similar to those of other studies (Bachmann et al., 2001). The average iron concentration in the samples taken from the field was 49.46 g/kg; these high iron concentrations form iron oxide (FeO) and iron hydroxide



**Fig. 2** Physical properties of soil and sediment samples

$\text{Fe}(\text{OH})_3$  precipitates along with silt and fine sand fractions in the textural structure of the sediments (Bachmann et al., 2001).

The average mineralogical composition of the Kuvashan mine site, and the tailings material transported from it via AMD, consists mainly of sulphates such as pyrite, jarosite, gypsum, alunite and goldichite (Kovenko, 1942; Yolcubal et al., 2023). Pyrite oxidation and many other reduction and oxidation reactions can frequently be observed in AMD processes (Nordstrom, 2015). The general reaction of the oxidation of pyrite that causes the formation of the material transported via AMD is given in Eq. 3. This mechanism explains the low pH and low lime percentage found in samples from the study area.



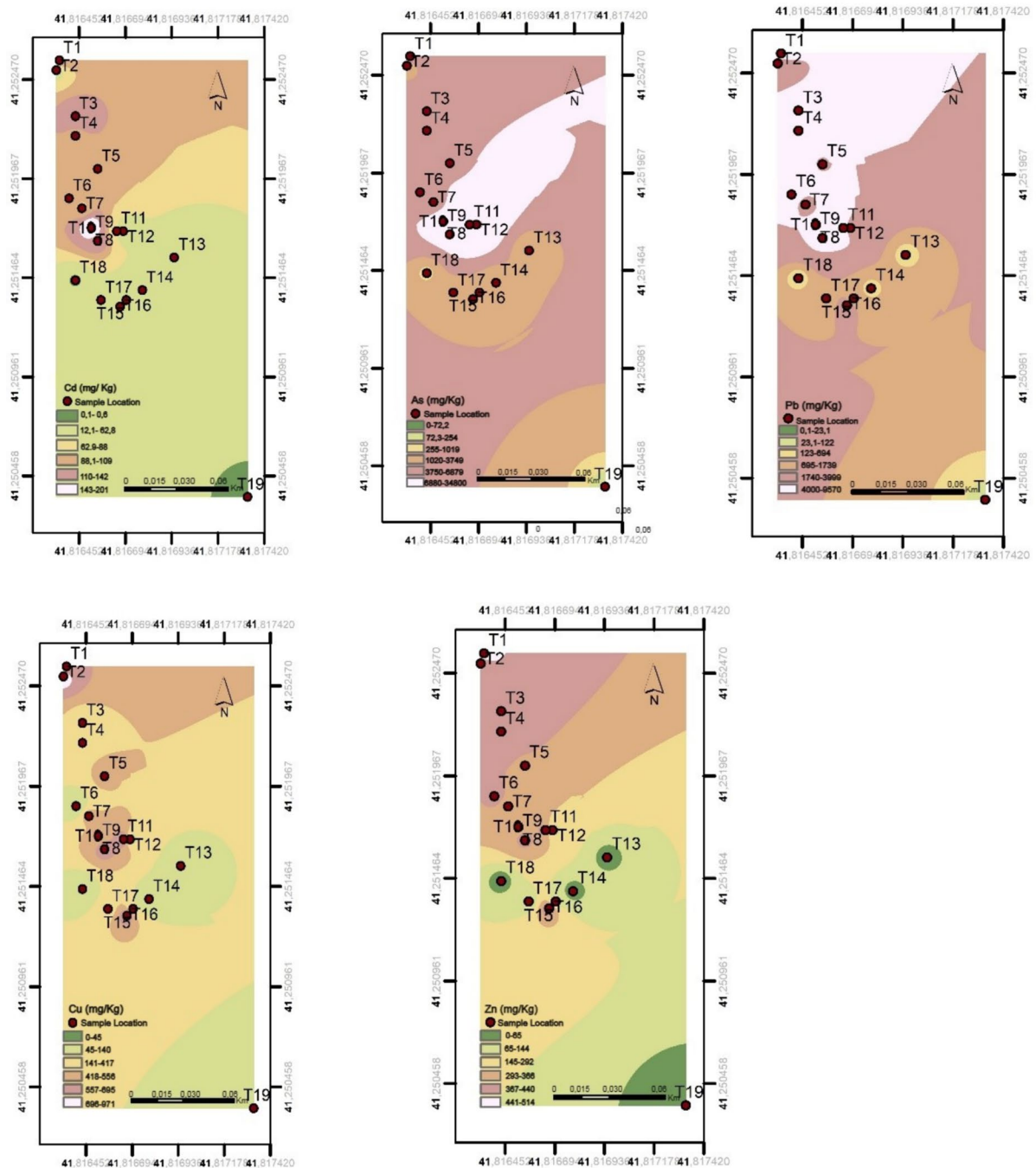
#### Metal content

Distribution maps of the trace elements concentrations in the soil, sediment, and water samples affected by AMD are given in Figs. 3 and 4, and

Fig. 5. According to the distribution map of trace elements in the soil samples, the metal concentrations were ordered by concentration as follows:  $\text{Fe} > \text{As} > \text{Al} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Mn} > \text{Cd} > \text{Cr} > \text{Ni}$ . In general, the highest total trace elements content among the soil samples was As ( $34,99 \text{ mg kg}^{-1}$ ), and was recorded at the KT11 sample point, where the mine tailings were stored; the highest Pb ( $9624 \text{ mg kg}^{-1}$ ), Cu ( $974 \text{ mg kg}^{-1}$ ), Cd ( $816 \text{ mg kg}^{-1}$ ) and Zn ( $435.80 \text{ mg kg}^{-1}$ ) concentrations were also detected at the K11 sample point (Fig. 3). All these substances are key trace elements.

However, the Ni, Mn, and Cr values in the samples taken from the field were found to be below the soil pollution limit values (Norrish, 1975). Table 1,

the data obtained are compared in to domestic and global soil pollution control regulations. The data from Table 1 shows that the Cd, Cu, Pb, and Zn values in the soil samples taken from the study area were above the limit values set by many countries.



**Fig. 3** Spatial distribution of trace elements in soil samples. \*The distribution map of other trace elements for soil samples is given in Suppl. Figure 3.

In addition, the average concentration of the trace element As, which has high toxicity in the trace elements ranking, was found to be  $5468.45 \text{ mg kg}^{-1}$  in

the study area. Other studies conducted to measure trace elements in soil samples taken from mining sites in different countries are presented in Table 2.

**Table 1** Background values of trace elements soil concentrations for some European countries (mg kg<sup>-1</sup>)

| Country                                 | Cu    | Zn    | Ni    | Cr    | Pb    | Cd    | Co    | Mn  | Fe     | Reference       |
|-----------------------------------------|-------|-------|-------|-------|-------|-------|-------|-----|--------|-----------------|
| Austria                                 | 17    | 65    | 20    | 20    | 15    | 0.20  | -     | 310 | 13.300 | Adriano, (2017) |
| Belgium                                 | 17    | 57    | 33    | 90    | 38    | 0.30  | 14    | 335 | 1638   |                 |
| Denmark                                 | 11    | 7     | 7     | 21    | 16    | 0.20  | 2.35  | 315 | 1236   |                 |
| France                                  | 13    | 16    | 35    | 29    | 30    | 0.70  | -     | 538 | -      |                 |
| Germany                                 | 22    | 83    | 15    | 55    | 56    | 0.500 | -     | 806 | 1147   |                 |
| Italy                                   | 51    | 89    | 46    | 100   | 21    | 0.50  | 16    | 900 | -      |                 |
| Netherlands                             | 18.60 | 72.50 | 15.60 | 25.40 | 60.20 | 1.80  | -     | 435 | -      |                 |
| Spain                                   | 14    | 59    | 28    | 38    | 35    | 1.70  | 0.60  | -   | -      |                 |
| Turkey<br>(East Black<br>Sea<br>Region) | 40.90 | 45.80 | 29.20 | 26    | 14.70 | 0.50  | 10.54 | -   | -      | DOKAP<br>(2018) |

As seen in Table 2, the soils in the Kuvarshan mine area have higher As and Fe concentrations than were found in studies conducted on mine soils in other countries. This situation shows the necessity of monitoring As, Pb, Cu, and Cd, among other trace elements that pose environmental risks. Studies have also shown that mineralization and rock mineralogy in the field provide information about the formation process, pollutant potential, and environmental pollution potential of AMDs (Lapakko, 2002).

Geological chemical analysis and X-ray diffraction (XRD) analysis of the Kuvarshan mining area's soil structure show that the mineralization is pyrite-dominant, with trace levels of sphalerite and minor hematite. Due to ore-rich pyritization in the field, the Kuvarshan deposit is defined as a Cu-type pyrite deposit. Such mineralizations contain sulphosalt (fahlerz) minerals with varying amounts of the main elements. These minerals commonly have the structure of tennantite ( $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{S}_{13}$ ) and contain up to 20% As by molecular weight, which explains the high concentrations of trace elements in the area of the Kuvarshan mine (Yolcubal et al., 2023).

As Fig. 4 shows, the average trace elements concentrations in the sediment samples taken from the areas exposed to AMD by the Kuvarshan mine area As (13363.7 mg kg<sup>-1</sup>), Pb (2912.5 mg kg<sup>-1</sup>), Cu (536.2 mg kg<sup>-1</sup>), Cd (332.60 mg kg<sup>-1</sup>) and Zn (269 mg kg<sup>-1</sup>). These findings show that the primary trace elements in the sediment samples are As, Pb, Cu, Cd, and Zn, as was found for the soil samples. This situation can be explained by the acidic environment formed as a result of the reactions involved in

AMD and the release and mobilization of trace elements such as As, Cd, Mn, Zn, Hg, Sb, Ag, Ni, and Mo from minerals such as pyrite, chalcopyrite, sphalerite, pyrrhotite and sulfates in the geological structure.

Studies conducted to measure trace elements in sediment samples taken from mining sites in different countries are presented in Table 3.

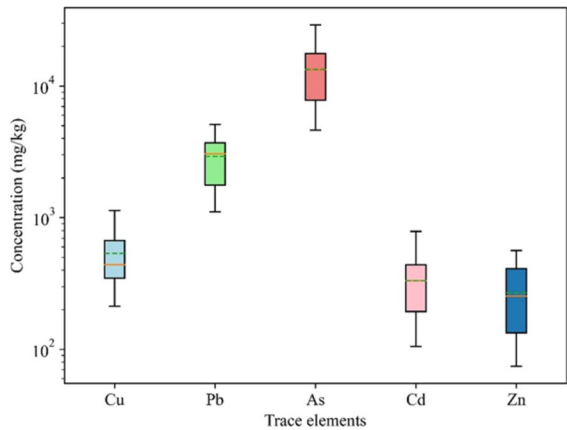
When the findings of this study are compared with the AMD-derived sediment samples found in other studies, while the Kuvarshan mine site has the highest concentrations of As and Cd, it also exhibits high concentrations of Pb and Cu. The results of water sampling in studies conducted to monitor the environmental effects of trace elements resulting from AMD are presented in Fig. 5.

\*The distribution map of other trace elements for water samples is given in Suppl. Figure 4.

When the distribution maps of the total concentrations of trace elements in the water samples were examined, it was determined that Cd concentration was 234.44 times higher than the limit value set by the US-EPA's freshwater quality criteria, As was 61.02 times higher, and Pb was 3.90 times higher. Ni concentration was determined to be within the limit values. When the average values of soil and sediment samples were examined, concentrations of the trace elements As, Cd, Pb, and Cu stood out. It has been determined that high concentrations of trace elements, especially those transported by AMD, result from the oxidation of sulphide minerals in the main rock structure. In this context, it is thought that pyrite ore, especially that found in the host rock, plays a role as the main mineral involved in AMD due to

**Table 2** Studies concentrations of trace elements in soil samples taken from mining sites in different countries (mg kg<sup>-1</sup>)

| Country "Mine Area"          | Cu     | Zn     | Pb      | As      | Cr     | Cd     | Ni    | Mn     | Al   | Fe    | Reference                     |
|------------------------------|--------|--------|---------|---------|--------|--------|-------|--------|------|-------|-------------------------------|
| Spain (Cabezo Rajeo)         | 332    | 12,500 | 8000    | 315     | –      | 41     | –     | 1508   | –    | 88.20 | Navarro et al., (2008)        |
| Spain (Madrid)               | 182.2  | 566.40 | –       | –       | –      | 8.68   | –     | 432.6  | –    | –     | Moreno-Jiménez et al., (2009) |
| China (Sichuan)              | 161.90 | 119.64 | 37.98   | –       | 232.50 | 1.52   | 89.46 | –      | –    | –     | Wu et al., (2021)             |
| South Korea (Myoungbong)     | 14     | 229    | 913     | 6670    | –      | 3.70   | –     | –      | –    | –     | Chang et al., (2005)          |
| Algeria (Médéa)              | 599    | 390.02 | 118.04  | 127.07  | 93.05  | –      | 58.01 | –      | –    | –     | Radi et al., (2022)           |
| Mongolia (Boroo)             | 23     | 24.20  | 19      | 265     | –      | 3.40   | –     | –      | –    | –     | Yoon et al., (2023)           |
| South China (Abandoned mine) | 40.91  | 269.69 | 77.12   | 11.23   | 72.37  | 0.91   | –     | 528.53 | –    | –     | Cao et al., (2023)            |
| China (Beijing)              | 534    | 46.21  | 2740    | 312     | –      | –      | 46.21 | 1770   | –    | –     | Jin et al., (2023)            |
| South Korea (Gijang)         | 205    | 249.70 | –       | 0.32    | 7.12   | 1.77   | –     | –      | –    | –     | Park et al., (2011)           |
| Mexico (San Felipe de Jesús) | 223    | 95.90  | 20.10   | –       | –      | –      | 786   | 786.90 | –    | 23.50 | Park et al., (2011)           |
| Turkey (Kuvarshan Mine)      | 455.64 | 261.79 | 2666.23 | 5468.45 | 25.85  | 121.28 | 11.36 | 181.77 | 5.38 | 95.82 | <i>This Study</i>             |



**Fig. 4** Scatter plot of trace elements in sediment sample

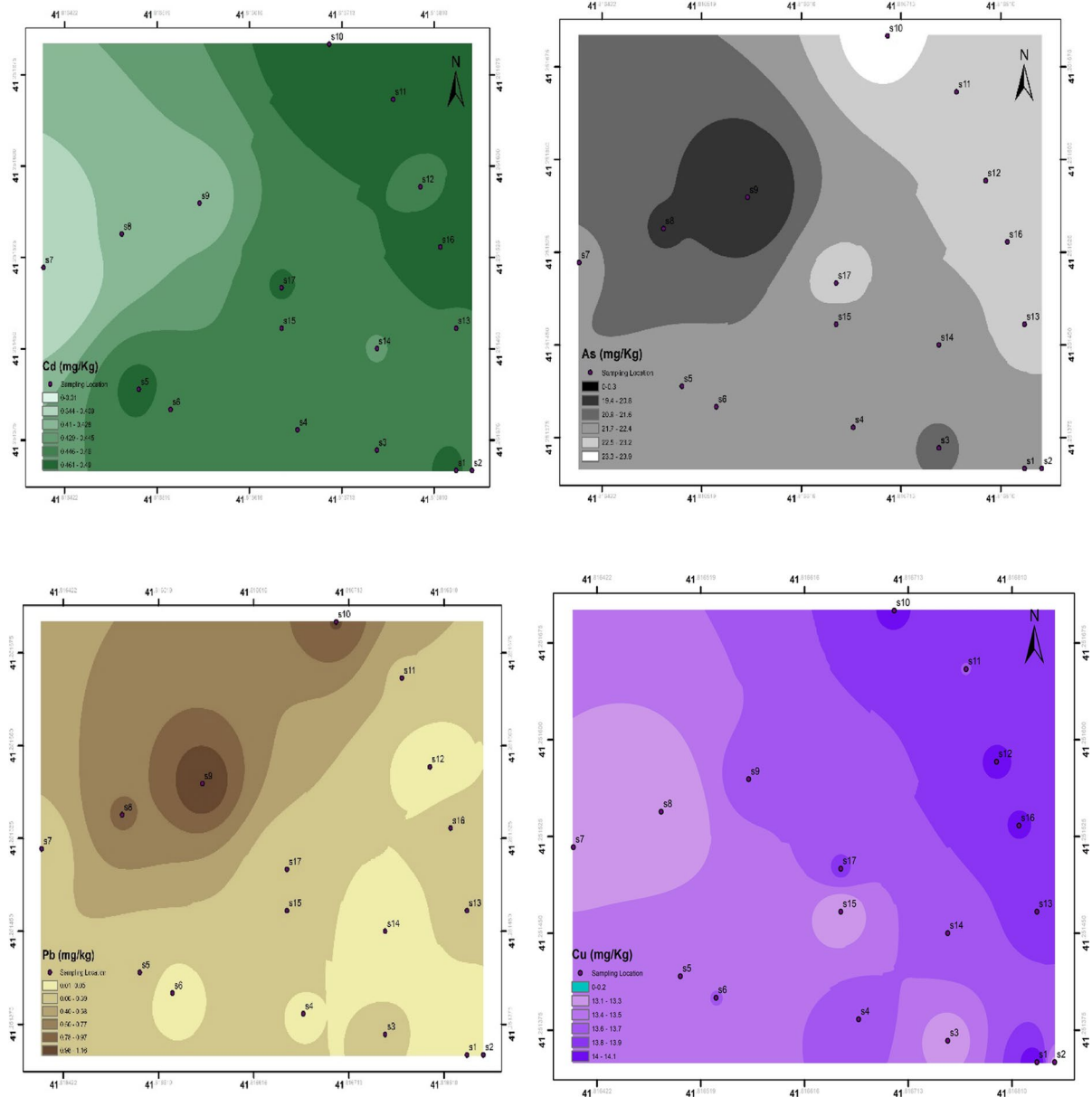
its interactions with oxygen, water and microorganisms (Blodau, 2006). Studies on the toxic effects of trace elements and their potential to mix with surface runoff and groundwater are presented in Table 4. The findings show that the main pollutant groups are closely related to the geological structure. Comparison of our findings with those of other studies conducted to monitor the environmental effects of AMD show that the Kuvarshan mine area is the most heavily polluted, in terms of As and Cu, of any of the areas considered.

Method validation

According to the results obtained in this study, recovery values for the total concentrations of each metal extracted from the certified standard (mean and standard deviation,  $n=3$ ) Sandy Loam Soil (Sigma Aldrich- CRM-027), Surface Water (SPS-SW2 Batch 135 Surface Water) and River Sediment ( LGC-6187) were between 62.59% and 100.2%. Repeatability or precision was calculated using relative standard deviation (RSD), which was found to be below 5% for all metals. These results demonstrate the suitability of the method chosen for the extraction in terms of precision and accuracy within the 95% confidence interval (Suppl. Table 3, Suppl. Tables 4 And Suppl. Table 5).

**Table 3** Studies conducted to measure trace elements concentrations contents in sediment samples taken from mining sites in different countries (mg kg<sup>-1</sup>)

| Country<br>(Mine Area)      | Cu      | Zn       | Pb      | As       | Cr      | Cd     | Ni     | Mn     | Al     | Fe     | Reference                   |
|-----------------------------|---------|----------|---------|----------|---------|--------|--------|--------|--------|--------|-----------------------------|
| Ethiopia<br>(Tigray Region) | 1535.20 | 17005.78 | 278     | 23.42    | 57.98   | 3.36   | 7.74   | -      | -      | -      | Habineza et al., (2023)     |
| China<br>(Zhejiang)         | 28.15   | 115.87   | 29.40   | -        | 55.46   | 0.13   | 45.07  | 954.98 | -      | -      | Zhao et al., (2023)         |
| Spain<br>(La Sierre )       | 4012.14 | 115.46   | 42.02   | 205.63   | 1311.92 | 1.52   | 427.23 | 938.53 | -      | 118.77 | Vasquez Ugaz et al., (2023) |
| Tunisia<br>(Lakhouat)       | 31.67   | 5789.9   | 3541.90 | 81.71    | 31.42   | 16.80  | 16.08  | -      | -      | -      | Ayari et al., (2023)        |
| Slovakia<br>(Gelnica)       | 268.6   | 177.5    | 219.30  | 500.94   | -       | 1.56   | -      | 566.6  | 56,750 | 12,257 | Singovszka et al., (2017)   |
| Turkey<br>(Kuvarshan Mine)  | 536.2   | 268.90   | 2912.50 | 13363.70 | 24.10   | 332.70 | 2.56   | 26.70  | 6410   | 49,400 | -                           |



**Table 4** Studies of trace elements concentrations in water samples taken from mining sites in different countries (mg L<sup>-1</sup>)

| Country<br>(Mine Area)     | Cu    | Zn   | Pb   | As    | Cr   | Cd   | Ni   | Mn   | Al  | Fe   | Reference                   |
|----------------------------|-------|------|------|-------|------|------|------|------|-----|------|-----------------------------|
| Serbia<br>(Beograd)        | 21.30 | 5.98 | –    | 0.14  | –    | –    | –    | 2.56 | –   | 77   | Atanacković et al., (2013)  |
| China<br>(Guangdong)       | 0.49  | –    | 0.17 | 0.03  | –    | 0.03 | –    | 0.17 | –   | –    | Luo et al., (2020)          |
| Spain<br>(Poderesa)        | 302   | 149  |      | 17.3  | –    | –    | –    | –    | 430 | 270  | Ruiz-Sánchez et al., (2023) |
| France<br>(Amous River)    | 0.13  | 9.0  | 0.6  | 1.0   | –    | –    | 0.2  | 6.0  | 240 | 230  | Casiot et al., (2009)       |
| Turkey<br>(Kuvashan Mine ) | 12.84 | 7.15 | 0.32 | 20.75 | 0.16 | 0.42 | 0.05 | 2.19 | 60  | 1179 | –                           |

Cu (0.73), Zn (0.6), Pb (0.86), As (0.95), Cd (0.95), EC (0.86), and salt (0.07). The locations of the samples representing the subpopulation suggest that PC1 represents As, Cd, Zn, Pb and Cd mineralizations related to structures such as pyrite, chalcopyrite, sphalerite, pyrrhotite and sulphosalts in the mine area (Yolcubal et al., 2023). In addition, monitoring studies conducted in the soil around abandoned mining areas suggest a one-way strong favourable effect on the total variance from mining. PC2 is characterized by positive loadings for Ni (0.86), Mn (0.64), Al (0.73), pH (0.58), and clay (0.9). The total of these components accounts for 15.68% of the total variance. Mn and Al obtained from the PC2 locations indicate the dominance of lithogenic elements at these sample sites (Anju and Banerjee, 2012). PC3 explains 11.09% of the total variance and is characterized by silt (0.97). This basic component is related to the textural composition of the soil structure. PC4 explains 6.9% of the total variance and is identified with positive loadings for CaCO<sub>3</sub> (0.93). The high concentration of lithogenic elements in the soil can again explain this composition.

#### Correlation matrix

Pearson correlation analysis determined the relationship between the trace elements in soil samples taken from the Kuvashan copper mine site. According to the findings show in Suppl. Table 7, there were high correlations between Pb and As (0.82), Zn and Pb (0.83), Cd and Pb (0.81), and Cu and Fe (0.85). These high correlations coincide with the relationship of metals in the geological structure and the results of

principal component analysis for PC1. The high correlations between Ni and Al (0.87) and between Mn and Al (0.80) coincide with the metal distribution due to the lithogenic structure defined by PC2 in the principal component analysis results.

Experimental findings show that AMD occurs due to the exposure of pyrite to atmospheric oxygen, water, and microorganisms. In particular, complex sulphur-containing minerals such as pyrite (FeS<sub>2</sub>), chalcopyrite (CuFeS<sub>2</sub>), and sphalerite (ZnS) in the geological structure of the mining area are considered to be the primary sources of mineral wastes. Many factors such as atmospheric oxygen, water, pH, mineral type, surface area, particle size and bacterial effect affect AMD, especially in the field (Daraz et al., 2023). AMD, which occurs due to these factors, begins a long process of environmental toxicity that is difficult to stop. This toxicity process is closely related to trace elements such as Pb, Cd, Cu, and As, which are some of the most toxic trace elements. The toxicity of Cd, Pb, and As in plants has severe effects on photosynthesis, plant growth, and biomass (Daraz et al., 2023).

When soil, sediment, and water samples from AMD in the Kuvashan site were evaluated together, it was found that the mineral wastes in the samples were closely related to the geological structure of the area. In particular, the mineralization of the Kuvashan copper mine, which has a pyritic Cu-type deposit form, has a structure which includes chalcopyrite, pyrite, and trace amounts of tennantite, making it necessary to monitor and treat it as an environmental risk, as these minerals contain high concentrations of the priority trace elements As, Cd, Pb, and Cu.

## Assessment of pollution in soil and sediments

Geo-accumulation index ( $I_{geo}$ ) values were calculated to evaluate the intensity of metallic PTE contamination in soil and sediment samples taken from the AMD area and its surroundings in the Kuvarshan mine site (Suppl. Figure 6). Average  $I_{geo}$  values for elements in the AMD-affected soil indicate that it is extremely highly polluted with As (8.35), Cd (7.95), and Pb (5.33), highly polluted with Cu (3.99), moderately polluted with Zn (1.39), and Mn, Fe, Cr, and Ni contamination was not determined. The average  $I_{geo}$  values of the elements in the AMD-affected sediment indicate that it is extremely highly polluted with As (11.92), Cd (10.86), and Pb (6.68), highly to extremely polluted with Cu (4.46), moderately polluted with Zn (1.51), while contamination was not determined for Fe, Cr, Ni, Al, and Mn.

CF values were calculated to evaluate As, Cu, Pb, Zn, Cr, Cd, Ni, Mn, Fe, and Al pollution levels in soil samples taken from the study area. The average CF values for trace elements in the soil samples indicate very high contamination for As (2734.2), Cd (1189), Pb (156.8) and Cu (31.9), significant contamination for Zn (5) and Fe (3.1), and little contamination for Cr (0.7), Ni (0.6), Mn (0.3), and Al (0.07). In the sediment samples, average CF values indicate very high contamination for As (6681.9), Cd (3261.7), Pb (171.3), and Cu (37.5), significant contamination for Zn (5.2), moderate contamination for Fe (1.6) and Cr (0.7), but little contamination for Ni (0.1), Mn (0.1), and Al (0.08). The magnitude of the trace elements pollution at the mine site varies depending on the type of waste. According to the average CF values, the most dominant pollutants in the collected soil and sediment samples were As, Cd, Pb, Cu, and Zn. The other statistical results conform to the results found in this analysis. High contamination levels in the AMD area and the surrounding soil and sediments in the Artvin Kuvarshan region pose a significant threat to environmental health and the ecosystem. Therefore, effective environmental measures should be taken to reduce this pollution and control its environmental impacts.

## Methods and recommendations used in AMD treatment

AMD is a widespread concern worldwide due to its strong acidity and toxicity. Treatment methods that are socio-economically and environmentally sustainable are urgently needed (Yang et al., 2023). The findings of previous studies have indicated that the release of high-potential toxic elements, such as Pb and As, is significantly elevated during the semi-arid period at the Kuvarshan mine site. However, the release of other metals has been observed to exhibit seasonal variation. Data on Multimeasurements of the release of trace elements in water samples made 2011 in order to monitor the environmental impacts of AMD originating from the Kuvarshan copper mine are presented in Suppl. Figure 5 (Yolcubal et al., 2023). When the data were examined, it was seen that the trace elements of water affected by AMD increased over time. The order of severity of this increase can be listed as  $Cd > As > Cr > Cu > Pb > Zn > Al > Ni > Mn$ . The increase in trace elements in AMD water is a result of the oxidation and leaching of waste materials from the closed copper mine into the soil and its passage to water resources through the soil and sediment. This process can cause environmental pollution, water quality decline, ecosystem disruptions, and potentially toxic effects that can harm human health. Therefore, various environmental management strategies are necessary to control and reduce these impacts of AMD.

Methods of purifying AMD can be categorised as active or passive. Active treatment involves the use of external energy or relies on chemical reactions, mainly neutralization precipitation, adsorption, ion exchange and membrane separation, precipitation, sulfate reduction, and ion exchange/absorption/filtration. These methods are mostly used for the treatment of AMD with medium to high flow rates and high acidity (Daraz et al., 2023). Passive treatment methods (e.g., constructed wetlands, anoxic limestone drains, open limestone channels, and sequential alkalinity generation systems) do not require a continuous input of chemical reagents and the secondary pollution effluent produced has a lesser impact on the environment (Silva et al., 2021; Xia et al., 2023). Adsorption is an active method that is faster and easier to use than the precipitation method. For this reason, it has

been preferred as an effective technique for trace elements removal (Ríos et al., 2008). Porous solids with large specific surface areas are used to remove trace elements from wastewater. Adsorbents used in trace elements removal include zeolite, mud, activated carbon/biochar, bentonite, wood ash, chitosan, agricultural wastes, and Schiff bases are frequently used in this context (Cegłowski & Schroeder, 2015; Ighalo et al., 2022; Katal et al., 2012; Xia et al., 2023). Given the physicochemical properties of Kuarshan copper mine wastes, Schiff bases, which plays a role in active methods for the treatment of AMD, especially in chemical reactions, can be used as an effective adsorbent for the precipitation and removal of trace elements. Schiff bases are inexpensive, and starting reagents such as aldehydes and ketones are readily available. Schiff bases can be synthesized with high yields in a simple process, and their properties can be easily tuned by carefully selecting reactants (Kaur et al., 2023). In addition, they form stable metal chelates and react with a number of metal ions such as copper (II), nickel (II), palladium (II), platinum (II), cobalt, iron, vanadium (IV) and zinc (II) (Khuwar and Lanjwani 1995).

In 2019, Konanç and Gümüş conducted a systematic study of the design, synthesis, and purification of ligands using a microcolumn technique that specifically binds trace elements and produces stable metal-ligand precipitates. This process provided that the chelation reaction was rapid and occurred at room temperature. In the study, the complexation of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Fe}^{3+}$  solutions added to pure water at a certain concentration was achieved with a rate of 89.6–99.6% through the complexation reaction with a Schiff base synthesized as a ligand (Konanç & Gümüş, 2019). Schiff base synthesized by Konanç et al. was adsorbed 47% for Cu, 71% for Cd, 85% for As and 94% for Fe in the analyses performed on water samples collected from acid ponds from mine wastes. Adsorption using Schiff bases is recommended as an active method for the treatment of AMD (Suppl. Figure 2).

## Conclusions

With a rapidly growing world population, global climate change is becoming more pronounced and available resources are rapidly diminishing. In particular, the environmental impact of abandoned mines is becoming increasingly important due to their potential impact on vital water resources.

AMD is becoming a serious environmental problem of anthropogenic origin due to the effects of its acidity and high concentrations of toxic trace elements. AMD is generally a result of the reactions between sulphide minerals, bound metal groups, oxygen, water and microorganisms.

Although the Kuarshan copper mine ceased operations approximately 75 years ago, it is a good indicator of the environmental effects of AMD caused by mining-related flotation wastes.

The findings show that closed mine sites still release high concentrations of trace elements. Analysis of the soil, water and sediment samples taken from the site show that the acidic geological environment of the site, which is a result of the oxidation of sulphide minerals in the main rock structure, supports metal release. Among the trace elements found at the site, As, Cd, Pb and Cu are among the priority pollutants.

Analysis of water samples collected for the study of AMD in 2011 and 2020 determined an increase in the concentrations of Cu, Zn, As and Al in these samples. This increase may vary depending on mineralogy and petrology, but the increase in these concentrations poses a serious risk for underground and surface flow waters, depending on seasonal conditions. Monitoring studies carried out in this context reveal the necessity of tracking and monitoring trace elements at the site through annual sampling (Suppl. Figure 5).

Since AMD poses an environmental problem, treatment as well as monitoring methods should be evaluated. Undoubtedly, the ultimate goal of all treatment methods is to minimize or eliminate environmental pollution. Active and passive methods applied in this context are still being developed; the aim is to ensure that these are sustainable, which can be supported through multidisciplinary collaboration. There is potential to use both active and passive treatment methods at the Kuarshan copper mine, but a cost and risk analysis may indicate that the use of the metal

chelation technique in addition to these methods may contribute to the

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## Declarations

**Conflict of interest** The authors declare no competing interests.

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