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Assessment of soil contamination by heavy metals and arsenic in Tamesguida abandoned copper mine area, Médéa, Algeria

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Abstract Heavy metal and arsenic pollution of soil remains a serious environmental problem long after mining operations have ended. For instance, the Tamesguida copper mine located in north-central Algeria has been abandoned for several decades without restoration or even an environmental impact assessment. Therefore, soils were collected from several locations in the vicinity of the old mine and tailings and analyzed for their Cu, Cr, As, Pb, Ni, Zn, and Fe rates to gauge the scope of the soil contamination caused by these elements, and assessing their origin and their dispersion in the mine area. High copper and arsenic contents were recorded in tailings and surrounding soils, far exceeding the world average shale, crustal average, and local soils. Except for lead, the spatial distribution of heavy metals and As shows a decrease in content as one moves away from the tailings, and the correlation matrix and PCA performed associate the origin of these elements with previous mining activities. The pollution indices, notably contamination degree (CD) and the pollution load index (PLI), categorize the site as a highly polluted area.

Keywords Pollution indices · Tailings · Impact · Spatial distribution · Gray copper · Metal sources

Introduction

Soils, a crucial natural resource for living organisms' survival and as agricultural support, are seriously threatened by various anthropogenic activities such as agricultural, sewage sludges, fossil fuel combustion, metallurgical industries, and especially metalliferous mining and smelting. Indeed, mining is a mainstay of the national

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economy. Nevertheless, most surface mining methods involve the removal of massive volumes of material to obtain the mineral deposit, and huge amounts of waste can therefore be generated during this process (Alloway, 1995; Bell & Donnelly, 2006).

Moreover, these generated wastes contribute to the degradation of the surrounding soil environment, which commonly accumulate in the vicinity of the mining operation and transform fertile soils into wastelands (Li, 2006). This often occurs without the local farmers' knowledge which reinforces the dangerousness of this insidious pollution. The mining operations remain polluting during the exploitation and even after the closure of the mine. These exploitations concerned several metals, and some of these metals such as copper (Cu) and zinc (Zn) are essential to life, but in high concentrations, they can be toxic (Allan, 1997). Copper ore mines and their processing have a drastically environmental impact, and the tailings found in large volumes that are residuals of the ore resulting from Cu extraction can lead to serious environmental risks because of the high toxicity of metals and metalloids that it contains, which can be transferred to aquatic and terrestrial ecosystems and affect soils, sediments, water, biodiversity, trophic circuits, and human health (Baycu et al., 2015; Rzymski et al., 2017).

Soil pollution by hazardous elements, especially copper, constitutes a major environmental issue, and their soil's contents are mainly dependent not only on the parent rock material but also on the soil's physicochemical properties (Kabata-Pendias, 2011) and soil's taxonomic order (Golia et al., 2019).

In this regard, several researchers have reported the metallic pollution of soils due to copper mines in numerous countries such as Bidone et al. (2001) in Brazil, Ettler et al. (2014) and Chileshe et al. (2020) in Zambia, Gałuszka et al. (2015) in Poland, Christou et al. (2017) in Cyprus, and Cheng et al. (2018) in China. However, few studies have been interested in pollution assessment in Algeria due to copper and mercury deposits such as Seklaoui et al. (2016) and Arab et al. (2021) in north-eastern Algeria.

Tamesguida, an ancient copper mine (Ni) formerly called Mouzaïa-les-mines, situated in north-central Algeria, was operative for more than a half-century where the mining activity had definitely ceased in 1963 without any rehabilitation for that site, and the generated tailings were dumped in an open area in the same site. This site has special importance because of its historical value for being the oldest mining concession in Algeria that has been exploited since 1844. As per the available literature, to date, no study has been done on the evaluation of soil contamination by mining wastes in the Tamesguida copper mine.

Fig. 1 Location of the Tamesguida mine site and localization of collected samples ▶

The objective of this study was to quantify the heavy metal and As content in the soils very close to the old mining site and also in the tailings in order to evaluate the contamination rate through the use of pollution indicators and deduce the probable source of pollution.

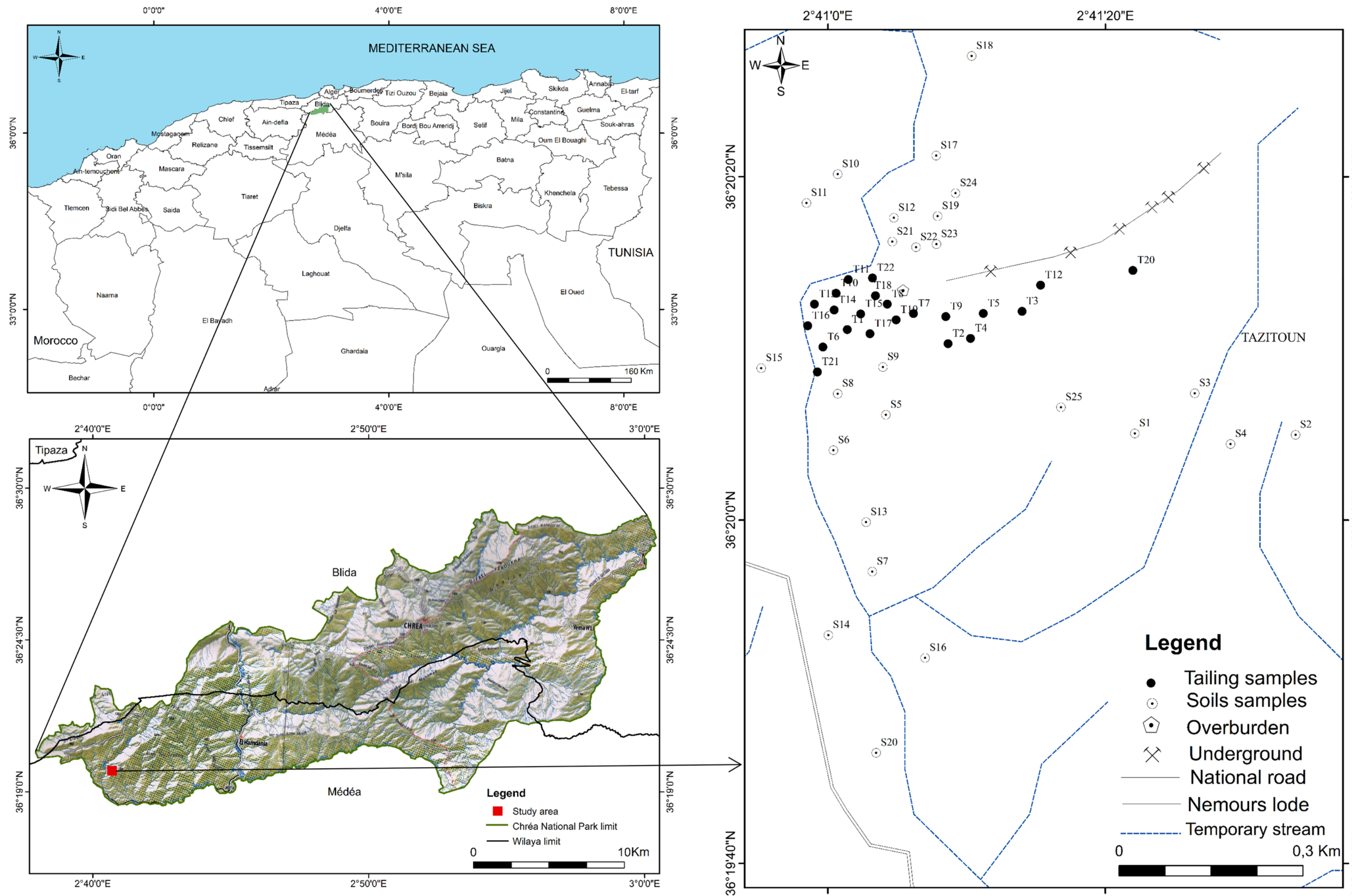
Materials and methods

Study area

This study was carried out at the Tamesguida copper mine area located at 36° 20′ 14″ N and 02° 41′ 03″ E in north-central Algeria at 80 km from Algiers (the capital) and close to Médéa city (about 15 km). It is situated on the Mediterranean matorral of Tamesguida mountain in the northwestern part of Chréa National Park (Fig. 1). The study area is located in a subhumid region at an altitude of almost 650 m. The climate of this area is Mediterranean, with a dry summer, warm temperate with an annual rainfall of 740 mm, mainly in winter, and the average annual temperature is about 15.90 °C. The dry season runs from mid-May to early September. The prevailing winds in this region come from the west on average, but they blow from the north during the dry period. The Tamesguida's copper mining lodes are mainly found in the schistose marls of the lower Cretaceous. The studied mine was exploited by open pit as well as by underground mining between the 1850s and 1900s. However, the mining was focused on extracting copper by open-cast mining in the later years of its activity before its closure in 1963. The ore minerals consist of chalcopyrite, pyrite, hematite, bornite, chalcocite, gersdorffite, and gray copper (isomorphic series between tennantite and tetrahedrite).

Soil sampling

Soils were sampled at several sites around the old copper mine (Fig. 1). Twenty-two samples were collected in tailings (T1 to T22), and twenty-five samples in the nearby surrounding soils (S1 to S25) where the local population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36°30'0"N
36°24'30"N
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36°20'0"N
36°19'40"N
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practice an agropastoral activity, two of which were taken from the overburden soils (S8 and S9). Furthermore, three soils (R1, R2, and R3) were collected away from the mining area in another site located in the South-East of mine at 2° 43′ 31″ E and 36° 19′ 34″ N in order to determine the local background. Soils were sampled from a depth of 15 to 20 cm at each site by a manual shovel, grinded in a nonmetallic mortar, air-dried, then sieved, and stored in a dark and dry place until analysis.

Physicochemical analysis

The pH was analyzed by pH meter using 1:5 soil–water according to Carter (2008), and the clay content was obtained through the particle-size distribution by soil sedimentation (Baize, 2000; White, 2006). Total Cu, Zn, Cr, As, Pb, Ni, and Fe were determined in soils and tailings by inductively coupled plasma-mass spectrometry (ICP-MS) using aqua regia for extraction, according to Zhang et al. (2017). A representative 1-g aliquot of the sample accurately weighed and introduced in a 250-ml beaker with a cover was digested by a mixture (1:2.5) of HNO_3 and HCl, then heated to 95 °C for 30 min in order to complete the acid attack and leading to some solution evaporation (3–4 ml). After cooling, the solution was diluted to volume with reagent water, mixed, and analyzed for elemental composition by ICP-MS thermo iCAP RQ. The detection limits (LoD) were 0.1671, 2.7636, 0.0146, 0.0106, 0.0196, 0.0168, and 1.1794 for Cu, Zn, Cr, As, Pb, Ni, and Fe, respectively.

Statistical analysis

Descriptive statistics (range, mean, confidence interval, and median) were determined for all soils for data interpretation. In order to deduce the relationships between heavy metal and As concentrations, pH, and clay content and identify the conjectural metal and metalloid source, Pearson’s correlation and principal component analysis (PCA) were performed using GraphPad Prism 9.

Assessment of pollution level

Many elementary methods can be employed to assess the soil pollution level. In this work, geoaccumulation index (Igeo), enrichment factors (EF), contamination factors (CF), degree of contamination (CD), and pollution load index (PLI) have been applied using the World Average Shale along with three local reference soils as background values.

Geoaccumulation index

Igeo was used to estimate the contamination level of samples and was calculated for the studied samples according to Müller (1969) (Eq. 1):

$$(\text{Igeo}) = \text{Log}2\left(\frac{Cn}{1.5Bn}\right) \qquad (1)$$

where Cn is the measured concentration of the studied element in the sample, Bn is the background value of the studied element, and 1.5 is used as a correction factor because of possible background variations due to lithogenic effects. Müller (1969) determined the descriptive categories for Igeo values, which are given in Table 1.

Enrichment factors

The enrichment factors (EF) used to detect anthropogenic inputs to metal and metalloid fluxes were calculated in this study according to Bourennane et al. (2010) and Odat (2015) in the following manner (Eq. 2):

$$EF = \frac{(\text{CM})}{(\text{CR})}\text{sample}/\frac{(\text{BM})}{(\text{BR})}\text{background} \qquad (2)$$

where [CM] and [CR] are the contents of the studied element and the reference element in soils or tailings, while [BM] and [BR] are the contents of the studied element and the reference element in the background. Thus, seven categories were determined (Table 1). The interpretation of the enrichment factor is based on the deviation of the ratio between the examined element and the reference element (Poh & Mohd Tahir, 2017). In this study, aluminum (Al), which has often been used to normalize trace element concentrations, was used as the reference element owing to its high natural concentration and minimal anthropogenic contamination and the fact that it is a structural element of the clay (Daskalakis & O’Connor, 1995; Rashed, 2010).

Contamination factor and contamination degree

The contamination factor (CF) and the contamination degree (CD) are used to evaluate the contamination level

Table 1 Igeo and EF categories

Geoaccumulation index			Enrichment factor		
Class	Value	Categories	Level	Value	Categories
0	$Igeo < 0$	Unpolluted	I	$EF < 1$	No enrichment
1	$0 < Igeo < 1$	Unpolluted to moderately polluted	II	$EF = 1–3$	Minor enrichment
2	$1 < Igeo < 2$	Moderately polluted	III	$EF = 3–5$	Moderate enrichment
3	$2 < Igeo < 3$	Moderately to strongly polluted	IV	$EF = 5–10$	Moderately severe enrichment
4	$3 < Igeo < 4$	Strongly polluted	V	$EF = 10–25$	Severe enrichment
5	$4 < Igeo < 5$	Strongly to extremely polluted	VI	$EF = 25–50$	Very severe enrichment
6	$5 < Igeo$	Extremely polluted	VII	$EF > 50$	Extremely severe enrichment

of pollutants in the studied site. The CF is obtained by dividing the concentration of each element in the sample (Cn) by the measured background values (Bn) according to Singh et al. (2017) by the following equation (Eq. 3):

$$(CF) = (\frac{Cn}{Bn}) \tag{3}$$

The contamination levels can be classified using the CF values according to Hakanson (1980) into four grades: $CF < 1$ with low contamination, $1 \leq CF < 3$ with moderate contamination, $3 \leq CF < 6$ with considerable contamination, and $CF \geq 6$ with very high contamination.

The CD was used to describe the level of contamination by each element and has been determined as defined by Ahdy and Khaled (2009). It corresponds to the sum of CF values of the studied site where $CD < 6$ shows a low degree of contamination, $6 \leq CD < 12$ is a moderate degree of contamination, $12 \leq CD < 24$ is a considerable degree of contamination, and $CD \geq 24$ indicates a very high degree of contamination indicating anthropogenic pollution.

Pollution load index

The pollution load index (PLI) is a potent and useful tool to assess the overall levels of heavy metal pollution, and it was determined using the procedure of Tomlinson et al. (1980) (Eq. 4):

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots CFn)} \tag{4}$$

where *PLI* is the pollution load index, *n* is the number of analyzed elements, and *CF* is the contamination factor previously calculated.

If PLI is greater than 1, there is pollution; otherwise, if PLI is less than 1, there is no pollution (Tomlinson et al., 1980; Varol, 2011).

Spatial mapping of heavy metals and As

The interpolation mapping of the spatial extent of heavy metals and As in the study area was realized from the sampled and analyzed points using the inverse distance weighting method (IDW) using ArcGis 10.4.

Results and discussion

Soil chemical analysis and heavy metal and As concentrations

The pH values, as shown in Table 2, chiefly indicate a neutral to slightly alkaline pH in all samples, with an average of 7.23 ± 0.13 for tailings and 7.05 ± 0.18 for surrounding soils. These rather high values are due to the calcareous nature of the parent rock. Indeed, the pH is one of the main parameters which has a meaningful influence on the mobility and toxicity of heavy metals in soils (Chuan et al., 1996). The average clay content in soils is approximately 35%; this high value is mainly due to type of soil in the study area which is a substratum on colluviums of marl and sandstone with scree in undeveloped soils of colluvial input and vertisols according to Pouget (1972).

The total average concentrations of heavy metals and As are shown in Table 2 for both soils and tailings. Copper concentrations in soils range from 88.73 to 1872.93

Table 2 pH, clay content, and heavy metal and As concentrations (mg kg^{-1}) in tailings, surrounding soils, and local soils

	Cu	Zn	Cr	As	Pb	Ni	Fe	pH	Clay%
Tailings (*n* = 20)									
Range	1033.3–8983.05	307.21–2003.14	37.39–117.7	303.57–1983.7	37.74–91.26	61.8–187.7	100,080–391,740	6.75–7.94	– –
Mean ± CI Median	3468.5 ± 737.87 3316.1	970.58 ± 173.06 983.4	87.46 ± 8.91 89.55	1230.98 ± 209.89 1131.65	64.92 ± 6.31 62.80	100.68 ± 11.81 104.22	239,126.46 ± 35,713.66 242,235	7.23 ± 0.13 7.22	– – –
Surrounding soils (*n* = 25) Range Mean ± CI Median	88.73–872.93 599.59 ± 234.05 392.02	7.86–968.9 390.02 ± 108.27 358.72	50.76–152.8 93.05 ± 13.89 80.88	21.48–253.9 127.07 ± 26.82 128.8	28.69–118.04 70.04 ± 11.69 62.93	16.99–118.74 58.01 ± 12.85 59.1	40,132–96,393 74,298.6 ± 6953.71 77,493	6.1–8 7.05 ± 0.18 7.03	25 40 34 ± 2.17 35
Local soil (*n* = 3) (LS) Mean ± CI	89.43 ± 6.72	269.29 ± 10.98	79.15 ± 5.59	24.4 ± 9.00	79.44 ± 11.69	76.73 ± 8.54	48,725.49 ± 2701.34	7.73 ± 0.13	30 1.96
WAS[a]	45	95	90	13	20	68	47,200	–	–
CA[b]	55	70	100	1.8	15	20	–	–	–
WHO[c]	36	50	100	–	85	35	–	–	–

[a] World average shale (Turekian & Wedepohl, 1961)

[b] Crustal average (Kabata-Pendias, 2011)

[c] WHO permissible limits for heavy metals in unpolluted soils

mg kg^{-1} with an average of 599.59±234.05 mg kg^{-1} which is almost 6, 11, and 13 times higher than local soils (LS), crustal average (CA), and world average shale (WAS), respectively. The highest Cu concentrations were recorded in soils near the overburden material (S8) and soils close to the tailing (S21 to S24), while the lowest contents were found in the soils furthest from the mine (S1 to S4 and S25). The decrease of the Cu contents depends on the distance from the pollution source, and Cu concentrations are indeed inversely proportional to the distance from the mine area; these results tie well with previous findings reported for other mining areas by Tembo et al. (2006) and Ettler et al. (2014) in Zambia and Punia et al. (2017) in India. As for tailings, high levels of Cu were found; they vary from 1033.3 to 8983.05 mg kg^{-1} with an average of 3468.5±737.87 mg kg^{-1} which is clearly superior than those of the local soils (38 times), crustal average (63 times), and world average shale (77 times).

Very high arsenic levels have been noticed in both surrounding soils with an average of 127.07±26.82 mg kg^{-1} and tailings with an average of 1230.98±209.89 mg kg^{-1}, which far exceeds the local soils, crustal average, and world average shale value. These high contents of As are undoubtedly related to the fact that the mined copper was found in gray copper ore in Mouzaïa-les-mines, especially in Nemours lodes, as mentioned by De Baudicour (1856). Indeed, the gray copper ore contains arsenic, antimony with copper and iron $(Cu, Fe, Zn, Ag)_{12}(Sb,As)_4S_{13}$ as indicated by Meunier et al. (2017), and during the roasting and smelting processes, arsenic, which is one of the major impurities in Cu concentrates, may be released causing environmental pollution (Díaz et al., 2018).

Moreover, the same general trend was observed for Fe, and its content is quite high, with an average of 239,126.46 ±35,713.66 mg kg^{-1} in tailings and 74,298.6±6953.71 mg kg^{-1} in soils against 47,200 mg kg^{-1} in world average shale and 48,725.49±2701.34 mg kg^{-1} in local soils. As for Zn, it turns out that its concentration is also high, with an average of 970.58±173.06 mg kg^{-1} in tailings and 390.02±108.27 mg kg^{-1} in soils versus 269 mg kg^{-1} in local soils, 70 mg kg^{-1} in crustal average, and 95 mg kg^{-1} in world average shale which suggests that this accompanying element in the mine might eventually be released during the mining process as explained by Qin et al. (2012).

The lead content shows an average of 70.04±11.69 mg kg^{-1} in soils and 64.92±6.31 mg kg^{-1} in tailings. Elevated lead levels in soils, rather than in tailings, suggest a different source of this metal than mining activities. Indeed, Pb in soils can eventually be originated from galena.

Statistical analysis

To correctly interpret our findings, a multivariate statistical analysis was carried out. The analysis of the correlation matrix in Table 3 between the pH and the abundance of heavy metals and As indicates a weak relationship between these values. However, as for the clay content, there is a strong positive correlation with copper (0.77) and iron (0.81) and a moderate correlation with arsenic (0.68). These results can be explained by the soils' taxonomic order according to Golia et al. (2019) who demonstrated that pH was the main parameter influencing the content of potentially toxic elements in alfisols, whereas clay content is the primary factor in vertisols.

For Cu, the correlation matrix in soils (Table 3) shows a strong positive correlation with Fe ($r=0.76$), which is also moderately correlated with As ($r=0.68$), Ni ($r=0.44$), Cr ($r=0.45$), and Zn ($r=0.47$) and a moderate correlation of Cu with Cr ($r=0.51$) and As ($r=0.43$). By the same token, the variables that have been selected for carrying out regressions and principal component analysis are divided into groups according to the correlation between them, and one principal component has been selected. A strong correlation between Cu, Fe, and As seems to be linked with the first component which explains 41.10% of the variance. Cotemporally, Cu is significantly correlated in tailings with As ($r=0.65$) and even better with Fe ($r=0.86$), which in turn is correlated with As ($r=0.52$). The PCA in Table 4 indicates that the only principal component which has been selected in tailings shows the same trend as soils for Cu, Fe, and As, which are strongly associated with 35.35% of the variance. It suggests similar origin (mining activities) and geochemical behavior of all these elements.

The main ore minerals in the Tamesguida copper mine are variable and consist, as shown mainly by the national geological and mining research office report of 1971, of hematite and limonite-baryte with traces of copper which occurs as traces of tetrahedrite, malachite, azurite, and chalcopyrite in addition to annabergite, gersdorffite, siderite, covellite, and goethite that were identified during our investigation. Thus, the source is tetrahedrite, azurite, covellite, chalcopyrite, and malachite for Cu; hematite, limonite, tetrahedrite, siderite, goethite, and chalcopyrite for Fe; and gray copper (tennantite) for As.

Assessment of pollution level

The mean Igeo values of Cu and As, as shown in Fig. 2, are around 2, which means that soils are moderately to strongly polluted using LS and WAS as background.

Table 3 Pearson's correlation coefficients among heavy metal and As concentrations, pH, and clay content in soils and tailings

	Cu	Zn	Cr	As	Pb	Ni	Fe	pH	Clay
Soils									
Cu	1								0.77*
Zn	0.08	1							0.38
Cr	0.51*	0.14	1						0.14
As	0.43*	0.41	0.13	1					0.65*
Pb	−0.22	0.33	0.37	−0.05	1				−0.32
Ni	0.11	0.11	0.08	0.30	0.16	1			0.20
Fe	0.76*	0.47*	0.45*	0.68*	0.07	0.44*	1		0.81*
pH	−0.29	0.32	0.12	−0.07	0.39	0.16	−0.22	1	−0.30
Clay	0.77*	0.38	0.14	0.65*	−0.32	0.20	0.81*	−0.30	1
Tailings									
Cu	1								
Zn	0.06	1							
Cr	−0.19	−0.41	1						
As	0.65*	0.24	0.02	1					
Pb	−0.03	0.16	0.02	−0.26	1				
Ni	0.04	−0.22	0.19	−0.03	0.06	1			
Fe	0.86*	0.20	−0.12	0.52*	0.25	−0.02	1		
pH	0.37	−0.12	0.07	0.08	0.06	0.09	0.34	1	

*Significant correlation at 95% confidence interval

Table 4 PCA of different heavy metals and As in soils and tailings

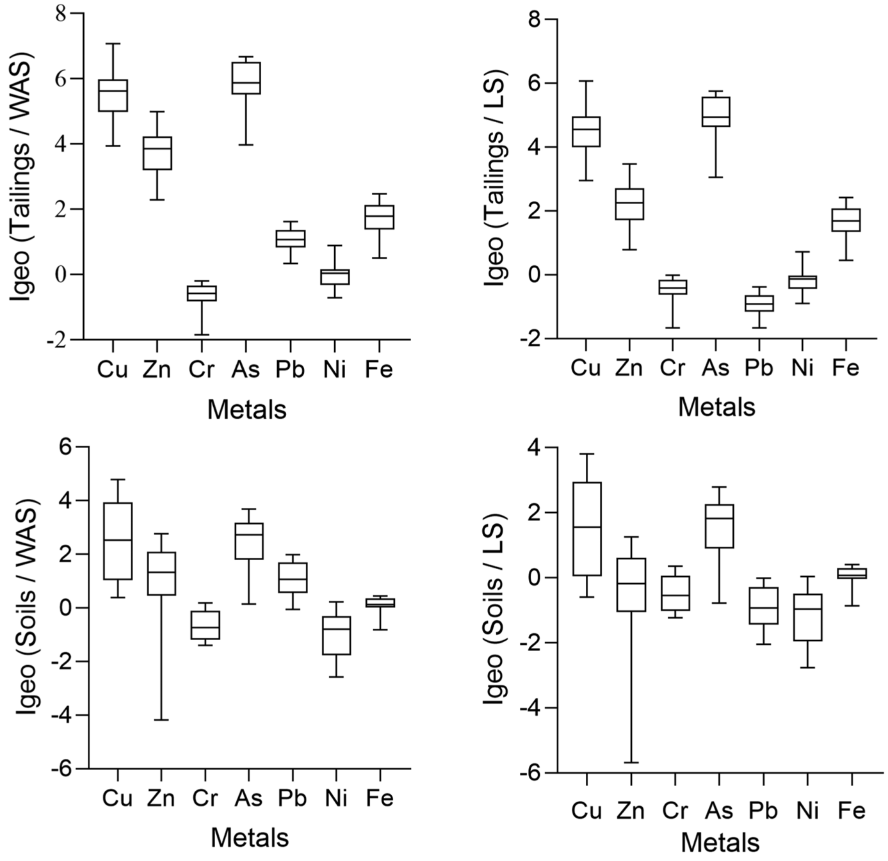
	Soils	Tailings
	PC 1	PC1
Cu	0.74*	0.91*
Zn	0.54	0.39
Cr	0.58	−0.30
As	0.75*	0.77*
Pb	0.17	0.03
Ni	0.46	−0.10
Fe	0.96*	0.88*
Eigen value	2.88	2.475
% of variance	41.10	35.35
Cumulative % of variance	41.10	35.35

*Significant correlation at 95% confidence interval

Indeed, the Igeo values for copper are similar to those found in several studies such as Punia et al. (2017) in India, Barkett and Akün (2018) in Cyprus, and Palanivel and Victor (2020) in Oman. However, the Igeo values of arsenic are particularly high in our study. Also, for Fe, the mean Igeo value fits in the unpolluted to moderately polluted category. For Ni and Cr, the average Igeo is lower than 0 and falls in the first category indicating that the soils are not polluted by these two elements using both LS and WAS as the background value. The same applies to Pb and Zn with average Igeo values less than 0, which means that these soils are unpolluted using LS, but they exceed 1 using WAS and class them as unpolluted to moderately polluted.

In tailings, the average Igeo value of Cu and As is nearly 5 using the LS as a background and exceeds 5 using the WAS as a background and falls therefore in the fifth and the sixth class, respectively, which means that they are strongly to extremely polluted. For Zn, the average Igeo value falls in the moderately to strongly polluted class using LS as a background, but its value approaches 4 using WAS as a background and falls in the strongly polluted category. As for Fe, the average Igeo value falls in the third class, and the tailings are considered moderately contaminated with Fe. At last,

Fig. 2 Igeo values of soils and tailings using WAS and LS as background



the Igeo values of Ni, Cr, and Pb are very weak and fall in the unpolluted category.

The pollution by heavy metals and As tends to be higher in the study area, and the average Igeo values were ranked in the following order Cu > As > Zn > Pb > Fe > Cr > Ni in soils and As > Cu > Zn > Fe > Pb > Ni > Cr in tailings. On the other hand, Cu presents high Igeo values among all the studied samples both in soils and in tailings, as found by Trevor et al. (2019), which hints that copper has been transferred from tailings and overburden to the soils as well as for arsenic.

The Cu's average EF value (Fig. 3) falls in the moderate to moderately severe enrichment categories for soils. As for Zn, it falls into minor to moderate enrichment categories, Pb into no to minor enrichment class, and finally Ni, Fe, and Cr into no enrichment category using LS and WAS as background values. In tailings, the results show high values of EF for Cu and As that fall in the sixth and seventh categories using LS and WAS, respectively, which correspond to very severe to extremely severe enrichment. As for Zn, the EF values vary between moderate enrichment to moderately severe enrichment according to the value of the background used. For Fe, the average EF value shows a moderate enrichment, and at last average EF values for Pb, Cr, and Ni indicate no to minor enrichment. These results are in accordance with Igeo values. The average EF value ranks heavy metals and As in the following order using the WAS as a background: Cu > As > Zn > Pb > Fe > Cr > Ni in soils and As > Cu > Zn > Fe > Pb > Ni > Cr in tailings.

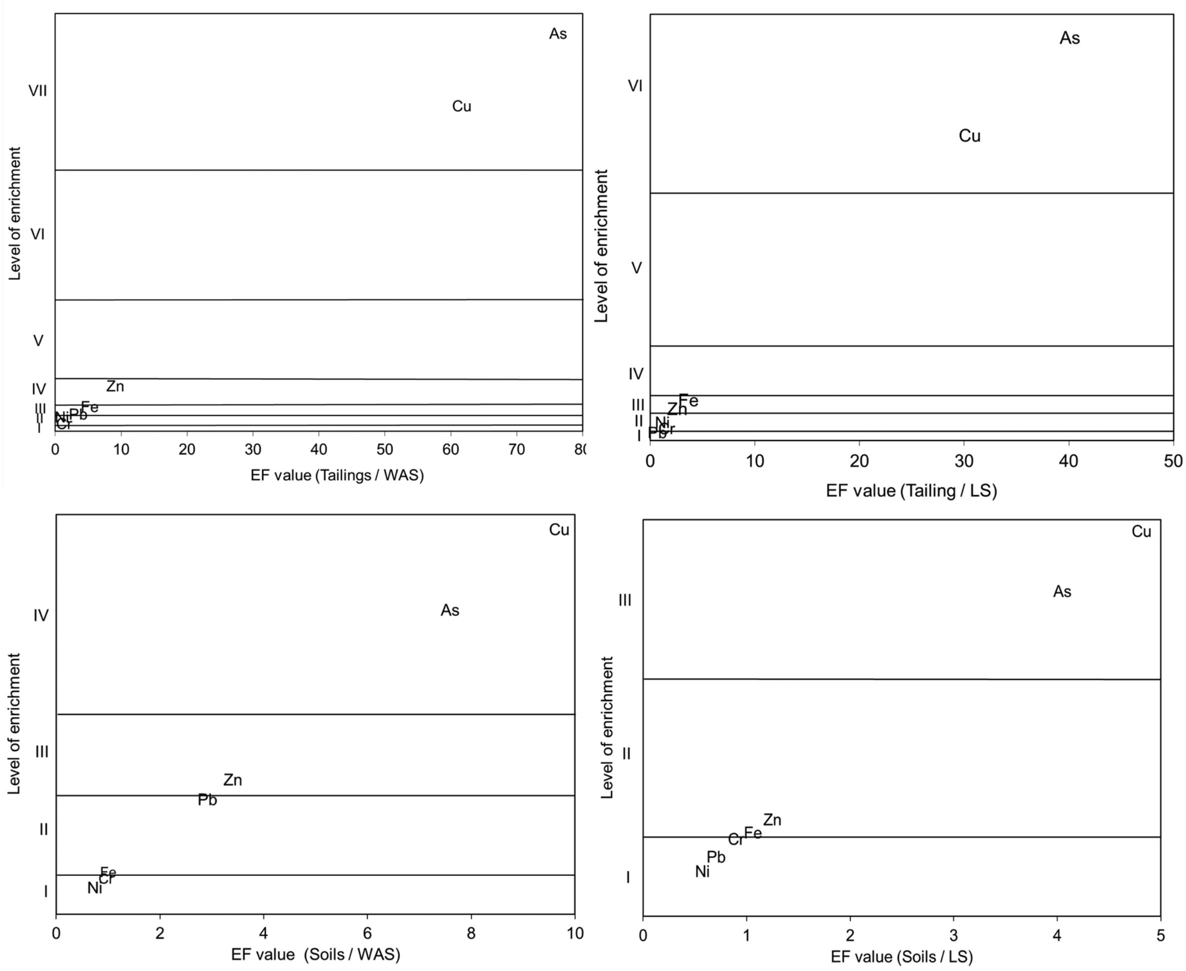


Fig. 3 Enrichment factor values of soils and tailings using WAS and LS as background

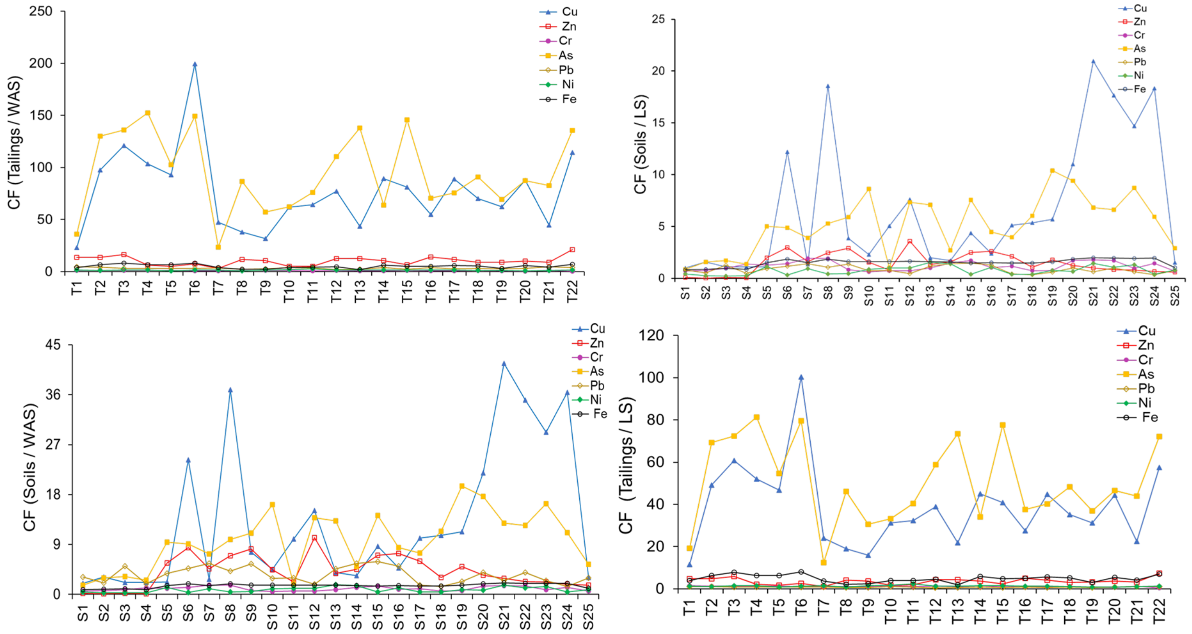


Fig. 4 Contamination factors in soils and tailings by heavy metals and As using WAS and LS as background

The most prevalent element in all studied locations is copper (Fig. 4); this finding is in line with previous studies by Covre et al. (2022) in Brazil, Barkett and Akün (2018) in Cyprus, and Giri et al. (2017) in India. The highest values of CF in soils were recorded in S21 to S24, S6, and S8, while the least worth was found in S1. As for arsenic, it is almost as common as copper, and its contamination factor values show very high contamination except for S1 to S4 with moderate contamination, S14 and S25 with considerable contamination. Moderate to considerable contamination for Pb was registered through studied soil samples, whereas low contamination was recorded in tailings not only for Pb but also for Ni and Cr. For Fe, Ni, and Cr, low to moderate contamination was registered in soils.

The results of the pollution load index in surrounding soils (Fig. 5) show that pollution exists in almost

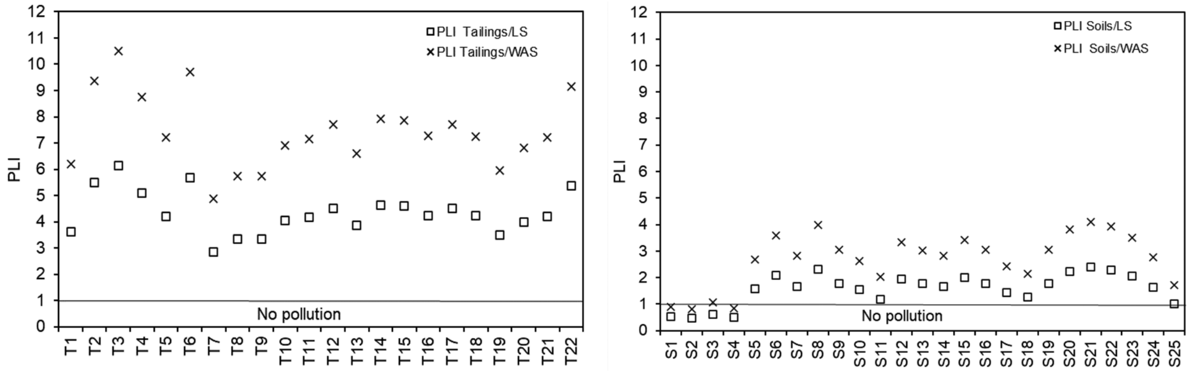


Fig. 5 Pollution load index values in tailings and soils using WAS and LS as background

all collected samples except S1, S2, S3, and S4, which are far from the pollution source with a PLI value lower than 1. PLI values reach their maximum in S21, S22, and S23 because of their proximity to the tailings. Likewise for S8 and S9, which are in close vicinity of overburden material and S20, S13, and S6 that are located under the north windward of the dry period as well as for S10, S11, and S15 that are influenced by alluvial sedimentary deposits. These findings are equally valid when using LS or WAS as a background value. As for tailings, all results show that PLI values are higher than 1 and reach an important value, especially when using the WAS as a background value, which means that the site is polluted.

The global evaluation of the level of contamination through the mean of the values of CF, CD, and PLI (Table 5) classifies the soils as polluted with an average value of PLI > 1 according to Tomlinson et al. (1980) as well for the tailings as for the surrounding soils. Similarly, for CD, the soils are designated very highly polluted with an overall average value that remains above 24 using WAS as a background. However, this site has a CD value of about 17 using LS as a background which qualifies the contamination of this site as considerable. The average CF values calculated for each studied element rank the level of contamination in the soils using WAS as background in the following order Cu > As > Zn > Pb > Fe > Cr > Ni and As > Cu > Zn > Fe > Pb > Ni > Cr in tailings.

Spatial distribution of heavy metals and As

Figure 6, which depicts the spatial distribution of the analyzed heavy metals and As, demonstrates that the highest concentrations of copper spread out mainly in the tailings and the vicinity of the lode from where it was mined. These concentrations appear to decrease with distance from the tailings, particularly in the northern and southern directions, but they remain significant, particularly in the western and eastern directions, which are impacted by the winds and alluvial deposits in this area. The distribution of As appears to follow a similar trend to that of Cu, as well as iron and zinc, implying the same origin and, most likely, the same transfer process of these elements from tailings to neighboring soils.

As for lead, according to its spatial distribution, it appears to have the highest concentrations away from the tailings and decreases in concentration as one gets closer to the mine site, showing that the source of this element is unrelated to the mining process.

Table 5 Average contamination factor (CF) with contamination degree (CD) and pollution load index (PLI) values of soils and tailings using WAS and LS as background

Studied element	Soil/WAS (CF)	Pollution status	Soil/LS (CF)	Pollution status	Tailing/ WAS (CF)	Pollution status	Tailing/ LS (CF)	Pollution status
Cu	13.32	Very high contamination	6.70	Very high contamination	77.08	Very high contamination	38.78	Very high contamination
Zn	4.11	Considerable contamination	1.45	Moderate contamination	10.22	Very high contamination	6.30	Very high contamination
Cr	1.03	Moderate contamination	1.18	Moderate contamination	0.97	Low contamination	1.10	Moderate contamination
As	9.77	Very high contamination	5.21	Considerable contamination	94.69	Very high contamination	50.45	Very high contamination
Pb	3.50	Considerable contamination	0.88	Low contamination	3.25	Considerable contamination	0.82	Low contamination
Ni	0.85	Low contamination	0.76	Low contamination	1.48	Moderate contamination	1.31	Moderate contamination
Fe	1.57	Moderate contamination	1.52	Moderate contamination	5.07	Considerable contamination	4.91	Considerable contamination
CD	34.17	Very high degree of contamination	17.70	Considerable degree of contamination	192.75	Very high degree of contamination	100.98	Very high degree of contamination
PLI	2,71	There is pollution	1.58	There is pollution	3.25	There is pollution	4.35	There is pollution

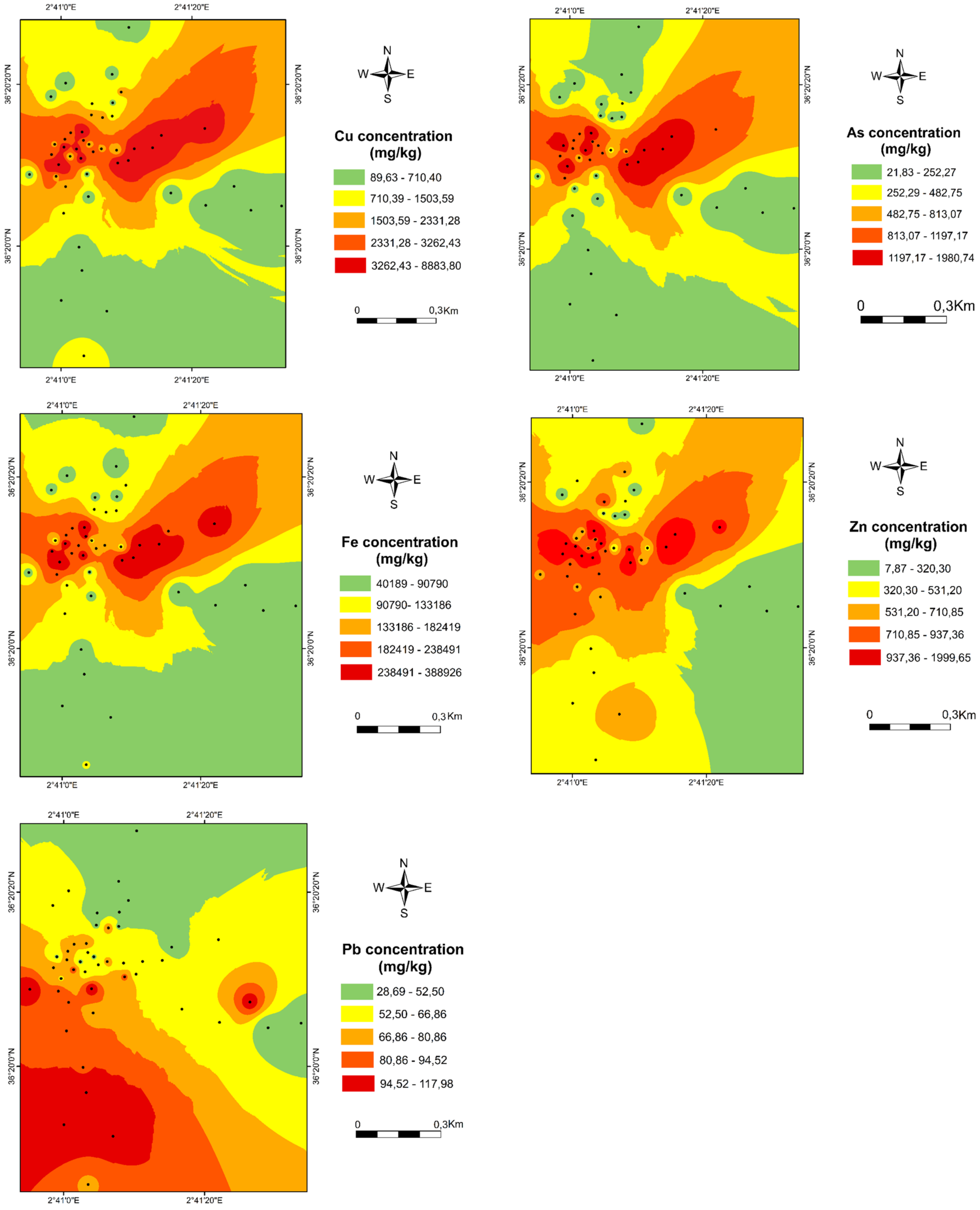


Fig. 6 Spatial distribution of heavy metals and As in the study area

Conclusion

In conclusion, the concentrations of heavy metals and As show significant variations among samples depending on their location and distance from tailings and overburden. Copper and arsenic concentrations far exceeded the LS, WAS, CA, and WHO values in most samples, except for those taken further away, which are also not influenced by wind input like the loess or alluvial sedimentary deposit. Cu concentrations were expected to be above average crustal abundances, as the study area is part of a Cu metallogenic area. The evaluation of contamination levels in the surrounding soils of the mine rates through various indices (Igeo, EF, CF, CD, and PLI) shows clearly that the obtained results using WAS as a background indicate more intense pollution than those obtained using LS; however, the trend remains the same even using LS, especially for As and Cu. They also classified metals in soils in the following order Cu > As > Zn > Pb > Fe > Cr > Ni. The level of heavy metals and As in soils is reasonably linked to past mining activities, especially since their levels are also high in the tailings, which enhances the hypothesis of their common source input, except in the case of lead, whose origin is different from the other studied elements. These high levels of pollution after nearly 60 years of activity cessation show the significant impact of copper (extraction) mining activity on the environment.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by NR, AH, and AB. NR wrote the first draft of the manuscript, and AH and AB commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

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