

# TRACE METALS ASSESSMENT IN SOILS AND SEDIMENTS NEAR THE ABANDONED MINE OF “EL ABED” Pb-Zn DEPOSIT, NORTHWEST ALGERIA

MELLAH, F.<sup>1,2\*</sup> – BOUTALEB, A.<sup>1</sup> – HENNI, B.<sup>1,2</sup> – BERDOUS, D.<sup>3</sup> – MELLAH, A.<sup>4</sup>

<sup>1</sup>*Algerian Laboratory of Metallogeny and Magmatism, FSTGAT, USTHB,  
BP 32 El Alia 16 111, Algiers, Algeria*

<sup>2</sup>*Department of Natural Sciences, ENS Kouba, Algiers, Algeria*

<sup>3</sup>*Faculty of Chemistry, USTHB, BP 32 El Alia 16 111, Algiers, Algeria*

<sup>4</sup>*COMENA, Frantz Fanon Center, Algiers, Algeria*

*\*Corresponding author  
e-mail: faridamellah@yahoo.fr*

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**Abstract.** The El Abed mining site in Algeria is one of the abandoned mining operations in northwest Algeria, leaving large amounts of mining waste accumulating due to wind erosion. This study aims to assess the pollution of the area and verify the concentrations and sources of trace metals in 56 surface environmental samples. Chemical analysis was performed using an iCAP 7000 Series ICP photoemission spectrophotometer. Environmental quality indicators (Igeo and EF using iron (Fe) and aluminum (Al) as references) and multivariate statistical methods with Geographic Information System (GIS) were used. In this study, we obtained the following mean values for trace metal concentrations: arsenic (As) = 30.82 mg/kg, Pb = 1219.27 mg/kg, Zn = 2855.94 mg/kg and copper (Cu) = 5.3 mg/kg. Based on these results, all trace metals except Cu exceeded the value of the geochemical background in the Earth's crust. The results of the multivariate analysis showed a strong relationship between Pb, Zn and As concentrations, which indicates that they are from human sources, and a weak relationship between the contamination indices for Cu, which is a natural source element. Many hotspots have been identified using GIS and based on spatial distribution maps, all sampling sites indicated general pollution, poor site quality and environmental hazards.

**Keywords:** *environmental media, geochemical indices, trace elements, mining, pollution, spatial distribution*

## Introduction

The world has witnessed many mining activities in the past years, and the exploitation of natural resources has led to abandoned historic mine sites (Hatar et al., 2013; Beane et al., 2016). The assessment of the pollution of areas of abandoned mines for surface samples or the pollution of areas affected by the mining industry is currently witnessing great development due to the emergence of new techniques in the field of scientific research. As for the research on pollution assessment in the El Abed area, it is the first research study to warn about the dangers of environmental pollution and its impact on human health. Furthermore, this study of local environmental problems is inspired by the growth of international awareness of environmental problems, which have become a major issue and concern of governments worldwide. Therefore, the environment must be preserved because it is the site of goods and services for humans (Dunlap et al., 1993; Frank et al., 2000).

Many studies have been conducted on the mining areas showing the great danger that trace metals pose to the environment and human health (Liu et al., 2013; Schnorr et al., 1995; Huang et al., 2017; Singovszka et al., 2020). Soil contamination with trace metals is a serious environmental problem as trace metals accumulate in the soil, are non-degradable and are transported and accumulated in living organisms through the food chain (Feng et al., 2009; Wcisło et al., 2016; Wang et al., 2017, 2018). There are two sources of trace metals, the human source, which represents the mining and fertilizer industries, and the natural source, which is the Earth's crust (Romic and Romic, 2003; Liu et al., 2005; Quan et al., 2015). Furthermore, these trace elements are carried by wind and water cycles (Han et al., 2018).

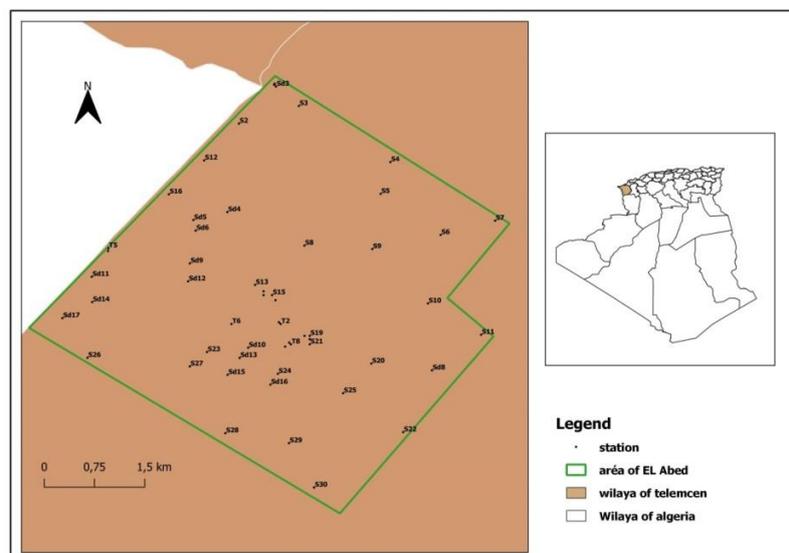
To identify sources and understand the spatial variability of trace metals in soils, their concentrations and spatiotemporal determination are studied. Determined chemical element concentrations are used to calculate pollution indices (Wang and Wang, 2020; Adnan et al., 2022). Among trace metals, we found arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) have high toxicity and cause environmental pollution (Xu et al., 2021).

The African continent is an important source of mineral resources globally, with the largest metal reserves (Bradshaw et al., 2010; Darimani et al., 2013). The South African countries became interested in the development of the mining industry due to the extensive exploitation of these sources, such as gold and diamonds (Mutemeri and Petersen, 2002). Similar studies in African sites at gold mining areas like the Bra River in Ghana showed toxic metal concentrations, including Pb, Zn and As, with high levels of pollution that are harmful to the ecosystem and can be transmitted to humans and animals (Asare, 2021). In several studies on contaminated sediment and soil samples, evidence has been provided that human interventions are a source of trace metal contamination (Jaffé et al., 2003; Shakir et al., 2017; Ali et al., 2019). Pb is a common soil pollutant from industrial waste and vehicular emissions from fuel and mining activities (Marzadori et al., 1996; Fayiga and Saha, 2016; Barsova et al., 2019; Zwolak et al., 2019). This element affects the intracellular calcium cycle, inhibiting several neurotransmitters and possibly causing cancer (Vijverberg et al., 1994; Tokar et al., 2011). In addition, Zn is a dangerous pollutant in the soil and travels through the food chain (Nahmani and Lavelle, 2002; Cordos et al., 2007; Klimek, 2012; Liu et al., 2013; Guarino et al., 2020). Extensive exposure to zinc chloride (ZnCl<sub>2</sub>) leads to respiratory disorders (Afshan et al., 2014). On the other hand, high concentrations affect agricultural soils and all organs, such as the liver and cardiovascular system and cellular respiration (Zhang et al., 2001; Tchounwou et al., 2003; Bakhat et al., 2019).

Algeria is one of the African countries that suffer from the pollution of abandoned mining areas. For instance, the El Abed mining area, located between Algeria and Morocco, is the largest extraction site for Pb and Zn in North Africa. The mine was exploited from 1948 until it was stopped in 2004, leaving waste in large quantities exposed to air and wind. For this reason, we decided to conduct an environmental study in the area to assess pollution and its effects on the ecosystem. Thus, the study was conducted for the following objectives (1) to evaluate the concentration and sources of trace metals in soils, sediments and mining wastes around the former El Abed Pb/Zn mine (northwest Algeria), (2) to assess the applied geochemical indicators (Igeo and EF) that include enrichment and human factors, and (3) to calculate and forecast the environmental risks of trace metals posed by the area by applying spatial analysis based on GIS.

## Study area

The study area is located in the northwest of Algeria between longitudes  $1^{\circ}40'W$  and  $1^{\circ}45'W$  latitude  $34^{\circ}25'N$  and  $34^{\circ}30'N$ , and finally to the west by the Moroccan border area, about 1 km away (Figs. 1 and A1).



**Figure 1.** The location of the El Abed region in relation to the map of Algeria and sampling sites

Geologically, the El Abed deposit is part of the Tlemcenian Domain. The Mounts of Ghar Rouban, and Sidi El Abed, constitute a mountain range which extends from Morocco to Algeria by forming a succession of Horsts and Grabens. It represents the eastern part of the Touissit-Boubker district, which is located in Morocco (Lucas, 1942; Touahri, 1987). It includes two structural units: a lower set consisting of Paleozoic terrains (formations sedimentary and volcanic, folded, metamorphosed and cut by magmatic occurrences) and an upper set formed by Mesozoic deposits (essentially Jurassic but strongly influenced by tectonics).

The prevailing winds blow in a westerly and southwesterly direction, with however southeasterly directions in January, February, June and August. The average annual wind speed is around 2.5 m/s, and the number of days with strong winds is about five per year.

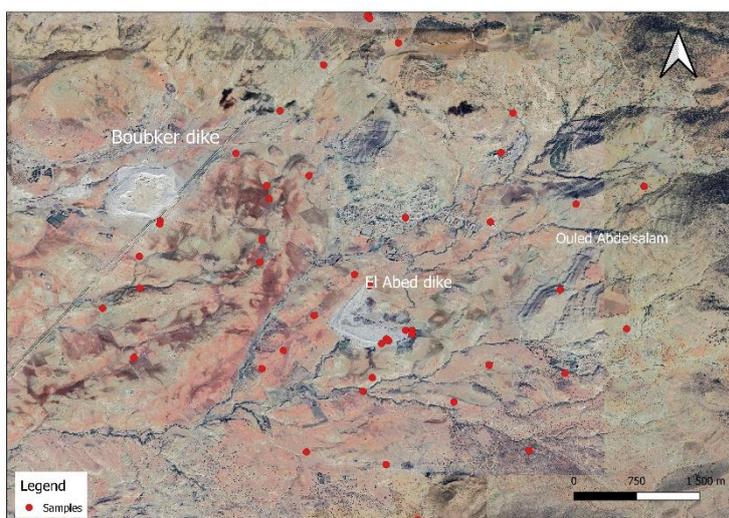
The climate of the region is of the continental type, characterized by a very prolonged cold winter and a hot and dry summer with temperatures varying from  $5^{\circ}C$  in winter to  $45^{\circ}C$  in summer. Precipitation is relatively low, with an interannual average of 300 mm unevenly distributed throughout the year (Azdimousa et al., 2011).

The study area is characterized by mountainous areas wooded with juniper and thuja. The agricultural activity practiced in the area is generally summarized by cultivating grains and trees (olive groves and apple trees). The El Abed deposit is the extension of an important mineralized layer, the eastern part of which is in Morocco (Touissit–Boubker). It was initially studied in Morocco, where the mineralization is exposed on the surface. It is the most important mineralization; it is hosted in the Dogger dolomites (Aéleno-Bajocien). The gangue is exclusively dolomitic; the mineralization occurs in

diffuse pockets or lenses, generally located near large breaks and often on small fractures. The mineral association is essentially composed of galena and sphalerite. Textures can be massive, banded and often brecciated. El Abed deposits contained 18 million tons of reserves at a rate of 5% Pb and 7% Zn from 1952 to 2001 (Boutaleb, 2001). Between 2010 and 2011, Boutaleb and Moussaoui conducted a petrographic and microthermometric study of dolomites and sphalerites, which showed that Pb-Zn mineralization was in stratiform clusters in the El Abed region (Boutaleb and Moussaoui, 2010).

## Materials and methods

Fifty-six (56) surface samples were taken from them (30 soils, 17 sediments and nine mining wastes) at several points in the El Abed area (roads, valleys, steep terrain, agricultural areas and a residential area) (*Fig. 2; Table A1*).



**Figure 2.** Surface of sampling sites of soils, sediments and mining wastes collected from El Abed area

All of the samples were collected randomly in April of 2017, including inside and near the waste mine, to assess the concentration of trace metals far from the mine (presumably uncontaminated) and more residuals from the Boubker mine on the Algerian-Moroccan border west of El Abed to assess the pollution of the area. The soil samples were mainly collected from 0 to 20 cm. At first, soils, sediments and mining wastes were dried at room temperature, then sieved at 400  $\mu\text{m}$  and grounded in a mortar previously disinfected with 96% ethanol. Furthermore, samples were sieved to obtain particles of less than 63  $\mu\text{m}$  (Hseu et al., 2002; Sakan et al., 2011). Then, 2 ml of 96% hydrofluoric acid (HF) and 9 ml of 40% nitric acid ( $\text{HNO}_3$ ) were added to soil and sediment samples. As for mining waste, we added 10 ml of hydrochloric acid (HCl) (37%) and 10 ml of HF (40%) to bottles and after waiting for a few minutes, the bottles were sealed (Buurman, 1996; Thomas et al., 2020). Next, the prepared samples were heated to 180°C in the microwave for 20 min. The bottles were then left to cool, and we added distilled water and filtered them to obtain 25 ml of the filtrate. The concentration

of the following elements: Pb, Zn, copper (Cu), As, Fe and Al was determined using an iCAP 7000 Series ICP-optical emission spectrophotometer at the Algerian Center for Nuclear Research (Algerian Atomic Energy Authority). The analytical method was used to neutralize trace metal concentrations by applying standard titration, actual addition recovery, and automated verification. As for the used reference materials, namely Pb, Zn, As and Cu (Plasma CAL ICP-OES Thermoscientific, USA) with a concentration of 1000 µg/ml + 4% HCl. Quality assurance and quality control tests were carried out in order to monitor and control the reliability of the analytical method. The limit of detection (LOD) and limit of quantification (LOQ) were calculated for the trace metals after the calibration curve. The performance characteristics of the ICP-OES calibration equation are given in *Table 1*. The equipment has been first calibrated with a multi-components standard solution (iCAP 6000 multi-element test solution manufactured under ISO9001 quality assurance system, Thermoscientific, USA). The ITEVA software considers optimized internal parameters involved in internal calibration. The measurements were performed in the same temperature conditions and the measurements’ standard deviations were automatically checked by the software and given as reliable output results.

**Table 1.** Performance characteristics of ICP-OES calibration equation

Trace metals	Parameters				
	R <sup>2</sup>	Slope	Intercepts	LODs (mg/kg)	LOQs (mg/Kg)
<b>Zn</b>	0.09	3838.13	486.84	0.00	0.00
<b>Pb</b>	0.98	171.06	-0.51	0.00	0.02
<b>As</b>	0.99	159.70	1.39	0.00	0.01
<b>Cu</b>	0.99	52.19	6.53	0.01	0.04
<b>Fe</b>	0.99	92.95	18.80	0.07	0.26
<b>Al</b>	0.98	1103.16	-45.61	0.01	0.02

We used multivariate statistical methods to analyze the data (descriptive analysis, Principal Component Analysis (PCA) and correlation analysis) to study the changes between the data and the obtained results. The software used was Excel Stat (2016 version), box plot data using Minitab 19.1, and the relationships between the analyzed elements were tested using Pearson’s coefficient with statistical significance set at  $P < 0.05$  by R.v 402 software. Values must be standardized with a transformation function to use parameters in multiple variables because they have different units of measurement (Medina-Gómez and Herrera-Silveira, 2003). As a result, the shape of the distribution of samples differs and the relationship between the parameters is determined by calculating Z, which is the normalization of the initial values (Lane, 2013).

$$Z = (x - \mu) / \sigma \quad (\text{Eq.1})$$

where Z is the standardized value, x indicates the original value of the measured parameter,  $\mu$  is the mean of the variable, and  $\sigma$  is the standard deviation.

Standardization was used to reduce the variance of variables and make the data dimensionless (El Yaouti et al., 2009; Hamzaoui-Azaza et al., 2011). The enrichment

factor was used to determine the sources of trace elements in the samples using a reference element (Li et al., 2017), and *Equation 2* (Buat-Menard and Chesselet, 1979) is given as follows:

$$EF = (C_n / C_{ref}) / (B_n / B_{ref}) \quad (\text{Eq.2})$$

where  $C_n$  is the concentration of the investigated element in the samples,  $C_{ref}$  is the concentration of the investigated element in the Earth’s crust.  $B_n$  is the concentration of the reference element in the samples, and  $B_{ref}$  is the concentration of the reference.

The reference element is the element whose content in the samples originated almost exclusively from the Earth’s crust, including Al and Titanium (Ti) (Schnorr et al., 1995; Reimann and Caritat, 2000). As reported by McLennan (2001), mineral concentrations were not available in deep soils. Thus, bedrock data were relied on and as the studied area was sedimentary, the Geochemical Background Values (GBV) were: 1.5 for As, 25 for Cu, 35000 for Fe, 80400 for Al, 17 for Pb and 71 (mg/kg) for Zn. Iron was chosen as the reference element for normalization due to its large abundance in the Earth’s crust and low occurrence variability (Krami et al., 2013). Fe and Al were used as reference elements for the calculation (Taylor and McLennan, 1995). The Geoaccumulation Index (Igeo) was evaluated based on the values suggested by Muller (1979). *Equation 3* indicates the Igeo calculation:

$$I_{geo} = \log_2 (C_i / (1.5 B_i)) \quad (\text{Eq.3})$$

where  $C_i$  is the concentration of each metal in the samples and  $B_i$  is the concentration of the same metal in the background.

This method allows the assessment of the extent of metal pollution into seven classes based on the increasing numerical value of the index (*Table 2*).

**Table 2.** Enriched factor (EF), geo-accumulation index (Igeo) range values and their environmental risk grades

Index type (single indices)	Value	Environmental risk grade	Reference
EF	0-1	Background concentration or no enrichment	Muller (1979)
	1-3	Minor enrichment	
	3-5	Moderate enrichment	
	5-10	Moderately severe enrichment	
	10-25	Severe enrichment	
	25-50	Very severe enrichment	
	>50	Extremely severe enrichment	
Igeo	0	Uncontaminated or background concentration	Muller (1979)
	0-1	Uncontaminated	
	1-2	Moderately contaminated to uncontaminated	
	2-3	Moderately contaminated	
	3-4	Moderately to highly contaminated	
	4-5	Highly contaminated	
	>5	Very highly contaminated	

Geochemical maps showing the overall spatial distribution of the El Abed area (soils, sediments and mining wastes) for the following trace metals (Pb, Zn, As and Cu) were generated using the ArcMap Spatial Analysis Tool (ArcGIS version 10.6, Esri Inc., Redlands, CA, USA). The inverse-distance-weighted interpolation method for predicting local features was performed to study the pollution of mining areas, especially local hotspots (Du Plessis, 2019; Kinimo et al., 2018).

## Results and discussion

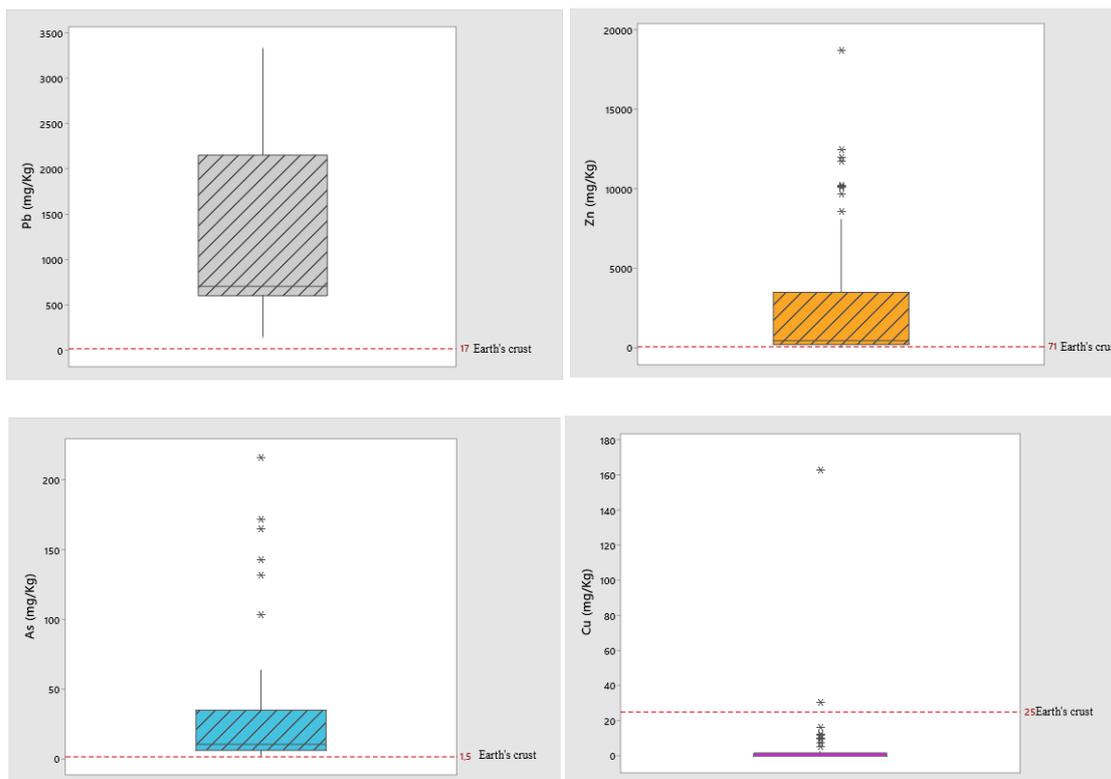
The metal concentrations among the 56 surface samples of soils, sediments and mining wastes were studied. The results of average concentration values for the studied metals were indicated in the following order: Zn > Pb > As > Cu (*Table 3*). Based on these results, all metals except Cu have exceeded the GBV of the Earth’s crust (McLennan, 2001).

**Table 3.** Statistical data for the concentrations of heavy metals for surface samples of soils, sediments and mining wastes, unit of mineral elements (mg/kg)

Variable	Observation	Min	Max	Medium	SD	Mean
Zn	56	59.05	18750	2855.93	4361.27	2855.94
Pb	56	147.625	3332.5	1219.27	930.21	1219.27
As	56	2.5	216.5	30.81	47.44	30.82
Cu	56	0	162.75	5.304	22.14	5.3

In addition, the values of Pb, As and Zn exceeded the European guideline values except for Cu, So, As exceeded the concentration threshold of 1.5, Pb concentration threshold exceeded 17, and zinc concentration exceeded 71 mg/kg, except that the average Cu concentrations are much lower than the concentration 25 mg/kg those found in the Earth’s crust (*Fig. 3*), which indicated a potential threat to the ecosystem in this region (*Table 4*). On the other hand, the study of Seklaoui et al. (2016) revealed important contamination by several metals such as Pb, Zn and Hg.

Thus, the results showed the presence of common characteristics for the samples and a difference between the trace metal concentrations of the soil, sediment and mining waste samples, so that the trace metal concentrations of the mining wastes (Zn = 5792.96, Pb = 2704.72 and As = 38.14 mg/kg) are greater than the trace metal concentrations of the soil (Zn = 2948.96, Pb = 1042.30 and As = 35.53 mg/kg) and sediments (Zn = 1136.85, Pb = 745.16 and As = 18.62 mg/kg). These differences confirm that the source of pollution is the waste from the mine, and it impacts the points of the neighboring and surrounding areas. As for the concentrations of trace metals in the sediments, they were low due to the presence of valleys and migration of trace metals. However, their concentrations remain high according to the values of the European guidelines (Zn = 100, Pb = 200, As = 5.9 and Cu = 100 mg/kg) and Earth’s crust (Zn = 71, Pb = 17, As = 1.5 and Cu = 25 mg/kg) McLennan (2001) (*Table 4*). The same results showed that the source of pollution and high concentration of heavy metals is the waste dump, which affected neighboring soil areas (Kanmani et al., 2013).



**Figure 3.** Box plot for trace metals (Pb, Zn, As and Cu) concentrations in the El Abed

**Table 4.** Mean concentration (mg/kg) of trace metals in El Abed area compared with other abandoned mining sites around the world and some published guidelines

Localization	Pb	Zn	As	Cu	Reference
<b>El Abed (Algeria) (n = 56)</b>	1219.27	2855.94	30.82	5.30	This study
<b>El Abed soil (n = 30)</b>	1042.30	2948.96	35.53	9.13	This study
<b>El Abed sediment (n = 17)</b>	745.16	1136.89	18.62	0.58	This study
<b>El Abed mining waste (n = 9)</b>	2704.72	5792.96	38.14	1.46	This study
<b>Azzaba waste (Algeria)</b>	1452.9	2337.1	198.4	NA	Seklaoui et al. (2016)
<b>El Kala soil (Algeria)</b>	203.34	294.01	NA	47.5	Arab et al. (2021)
<b>Songcheon mine tailing (Korea)</b>	20.32	3059	51.41	385	Lim et al. (2008)
<b>Zaida tailing (Morocco)</b>	1872.9	91.1	NA	47.7	Baghdad et al. (2006)
<b>Guarapiranga reservoir sediment (Brazil)</b>	NA	40.8	4.9	NA	Guimarães et al. (2011)
<b>Voghji river (water and sediment) (Armenia)</b>	11.5	41.4	6.93	119	Gabrielyan et al. (2018)
<b>England and Wales</b>	81	91	2	24	Rawlins et al. (2012)
<b>Canadian guidelines</b>	27	200	12	63	CCME (2007) <sup>a</sup>
<b>World soils</b>	27	70	NA	38.9	Kabata-Pendias (2011)
<b>Vosges or the Cevennes soil (France)</b>	30.4	68	NA	17.4	Baize et al. (2007)
<b>European guidelines</b>	100	200	5.9	100	Leschber et al. (2006) <sup>b</sup>
<b>Earth's crust</b>	17	71	1.5	25	McLennan (2001)

NA: not available; n: number of samples

<sup>a</sup>Canadian soil quality guidelines for the protection of the environment and human health

<sup>b</sup>Threshold or guideline values in European soil and sewages sludges (pH > 7)

An abandoned mine area in South Korea was studied and the results indicated that the average concentrations of trace metals exceeded the national limits in farmland soils for As, Pb, Cd, and Zn with 5.99, 76.2, 0.88 and 128.3 mg/kg, respectively (Yun et al., 2020). Another study was carried out in the wetlands of Liupanshui Minghu, an industrial and mining area, by measuring the concentrations of trace metals like Pb, Zn and Cu in surface deposits. The average concentrations were 197, 222 and 59.1 mg/kg, respectively (Yu et al., 2021). The concentration of Pb, Zn and Cu in an abandoned mine tailing in the region of High Moulaya (Eastern Morocco) was determined and the average concentrations were as follows: Pb = 1872.9, Zn = 91.1 and Cu = 47.7 mg/kg, respectively.

The obtained Pearson correlation coefficients of the trace metals for surface samples of El Abed region are presented in *Table 5*. A strong and significant positive correlation was found at  $P = 0.05$  between Pb and Zn ( $r = 0.87$ ) and As and Pb ( $r = 0.70$ ). After using  $P < 0.05$  to analyze the correlation coefficient between the studied trace metals, some pairs of trace metals had a significant positive relationship. The results showed that Pb has a strong association with trace metals, indicating that the origin of trace metals is waste (Kumar and Fulekar, 2019). The results of the study conducted in Slovakia, by comparing the degree of pollution between two time periods (1997 and 2015), before and after the end of mining activities after using Spearman’s correlation analysis that Hg had a significant positive relationship with all trace metals except for Pb and Cd, between Ni and Cu ( $r = 0.75$ ,  $P < 0.05$ ) and no significant correlation was found for As (Demková et al., 2017). In the study of Chen et al. (2014), there were significant correlations between the history of the parks and the concentrations of Cu (correlation coefficient: 0.580,  $P < 0.01$ ) and Pb (correlation coefficient: 0.628,  $P < 0.001$ ).

**Table 5.** Correlation matrix of trace metals for surface samples of El Abed region

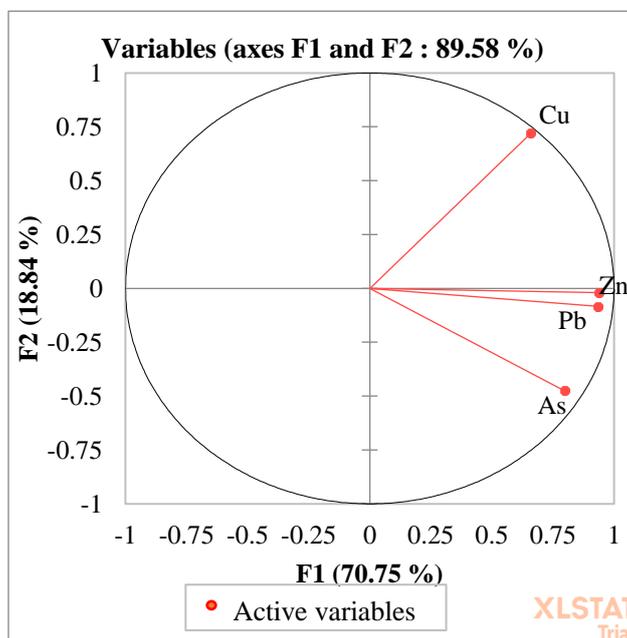
Correlation matrix (Pearson ( <i>n</i> ))				
Variables	Zn	Pb	As	Cu
Zn	<b>1</b>			
Pb	<b>0.87</b>	<b>1</b>		
As	0.68	<b>0.70</b>	<b>1</b>	
Cu	0.55	0.51	0.26	<b>1</b>

Values in bold are different from 0 at significance levels higher than 0.7 at  $\alpha = 0.05$

The PCA for concentrations of trace metals obtained for surface samples of the El Abed area are shown in *Figure 4*. The graphical interpretation of PCA results is mainly carried out according to the first and second plans. The first plan provides the maximum information with a contribution of 89.58% for the overall variance. Along axis 1, with a variability of 70.75% it is presented by the parameter Zn with a contribution of 31.19, and axis 2, with a variability of 18.84% presented by the parameter Cu with a contribution of 69.00.

We noticed a clear differentiation between the two distinct groups. The first group included a factor (Cu) with positive values on the first axis (F1) and the second axis (F2). The second group has three factors (Pb, Zn and As) that have positive values for F1 and negative values for F2. We explain that the factors Zn, Pb and As are closely and

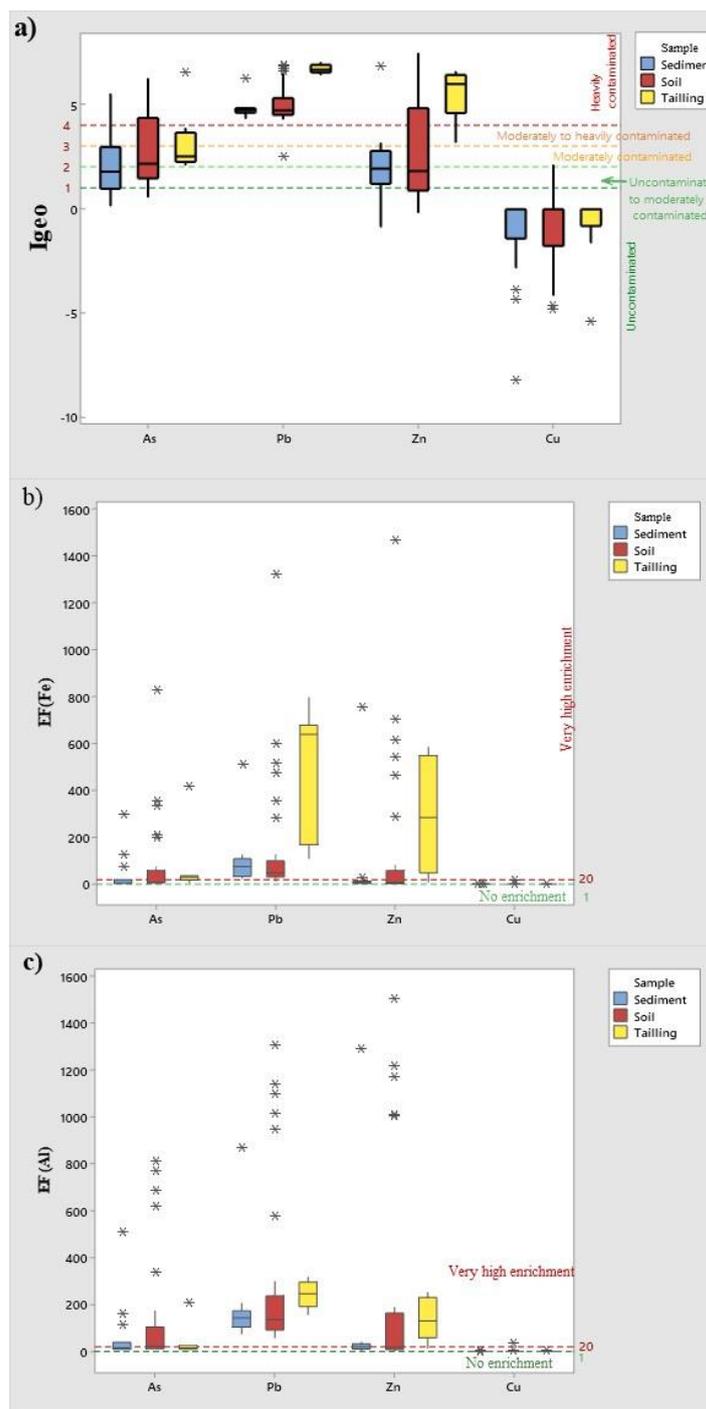
positively related to F1, which means that they have a common idea that unites them, and Cu is closely related to F2 and this indicates that the more different the factor Cu differs from the other factors. The results of the study conducted on Pb and Zn mining areas in India showed that the multivariate analysis provided an important tool for the distribution of sources, and it was noted that trace metals could have a human origin (Anju and Banerjee, 2012). In our case, multiple variables identified important and obvious groups of trace metals (Pb, Zn, As and Cu) for the surface samples, the heavy metal bond, indicating that they are of human origin.



**Figure 4.** Representation of the results of the analysis of the main component of the surface samples of El Abed area projecting the variables (trace metals) on the level F1-F2

The results of the Igeo mean for trace metals and the classification of their values according to their degree of environmental risk showed that the mean Igeo (As) and Igeo (Zn) range between 2-3, meaning they are moderately contaminated, while Igeo (Pb) exceeds 5, which is very highly contaminated, with the exception of Cu, which is less than 0, meaning uncontaminated. The order of trace minerals ranges as follows: Based on Muller (1979). The results also showed that the percentage of pollution in mining waste and soil is high for trace metals (Pb, Zn, and As), while the sediments are classified as moderate to uncontaminated for all trace metals (Fig. 5a). The same results in northeastern Morocco, the Sebou River, showed that 60% of the sediment samples were contaminated such that ( $1 < Igeo \leq 2$ ) for the trace metals Cu and Pb (El Mrissani et al., 2021).

Showing EF results using two references for iron and aluminum, for trace metals such as Pb, Zn and As greater than 50, they are classified as very high enrichment for the server, while the EF for Cu ranges from 0-1, so Classified as no enrichment (Fig. 5c and b). Enrichment factor values for surface soils of an agricultural area in Bangladesh ranged from 100% EF values to 1.5 for Zn, Pb, Cd and Cu, indicating significant enrichment with man-made trace metals (Bushra et al., 2022).



**Figure 5.** Box plot for mean geoaccumulation index ( $I_{geo}$ ), mean enrichment factors ( $EF$ ) with iron and aluminum references for trace elements (Pb, As, Zn and Cu) in the studied soil, sediment and mining waste samples of the region El Abed (classification reference values shown by horizontal dashed lines)

Pearson’s correlation coefficients were obtained for the correlation matrix of contamination indices for El Abed surface samples (Table 6). A strong and significant positive correlation was found at  $P = 0.01$  between  $EF(Fe)$  Pb and  $EF(Fe)$  Zn ( $r = 0.95$ ),  $EF(Al)$  Zn and  $EF(Al)$  Pb ( $r = 0.95$ ),  $EF(Fe)$  Cu and  $EF(Al)$  Cu ( $r = 0.95$ ),  $EF(Fe)$  Zn and

EF(Al) Zn ( $r = 0.94$ ), EF(Fe) As and EF(Al) As ( $r = 0.91$ ), EF(Fe)Zn and EF(Al) Pb ( $r = 0.90$ ), EF(Al) Zn and Igeo Zn ( $r = 0.87$ ), EF(Fe)Pb and EF(Al)Zn ( $r = 0.86$ ), EF(Al) As and Igeo As ( $r = 0.83$ ), EF(Fe)As and EF(Al) Pb ( $r = 0.81$ ), EF(Fe)As and EF(Fe) Zn ( $r = 0.80$ ). Also, a moderate relationship between Igeo As and Igeo Zn ( $r = 0.61$ ), EF(Al) Zn and EF(Al) Cu ( $r = 0.60$ ), EF(Fe) Cu and EF(Al) Zn ( $r = 0.55$ ), EF(Al) Pb and EF(Al) Cu ( $r = 0.55$ ), EF(Fe) Cu and EF(Al) Pb ( $r = 0.54$ ), EF(Fe) Cu and Igeo Zn ( $r = 0.48$ ), EF(Al) Cu and Igeo Pb ( $r = 0.48$ ), EF(Fe) Zn and EF(Fe) Cu ( $r = 0.43$ ), EF(Fe) Pb and EF(Fe) Cu ( $r = 0.40$ ), EF(Fe) Pb and EF(Al) Cu ( $r = 0.38$ ). There is a negative relationship between EF(Al) Cu and Igeo Cu ( $r = -0.066$ ), Igeo As and Igeo Cu ( $r = -0.02$ ), Igeo Zn and Igeo Cu ( $r = -0.07$ ). Negative and inverse correlation between Cd and Fe reveal that these metals are derived from different sources (Laribi et al., 2017).

**Table 6.** Correlation coefficients between pollution indicators ( $EF_{(Fe)}$ ,  $EF_{(Al)}$  and Igeo) of trace metals (Pb, Zn, As and Cu) detected in surface samples of the selected study sites

Correlation matrix (Pearson)												
Variables	EF(Fe) As	EF(Fe) Pb	EF(Fe) Zn	EF(Fe) Cu	EF(Al) As	EF(Al) Pb	EF(Al) Zn	EF(Al) Cu	Igeo As	Igeo Pb	Igeo Zn	Igeo Cu
EF(Fe)As	<b>1</b>											
EF(Fe)Pb	<b>0.80</b>	<b>1</b>										
EF(Fe)Zn	<b>0.80</b>	<b>0.95</b>	<b>1</b>									
EF(Fe)Cu	0.20	0.40	0.43	<b>1</b>								
EF(Al)As	<b>0.91</b>	<b>0.73</b>	<b>0.73</b>	0.29	<b>1</b>							
EF(Al)Pb	<b>0.81</b>	<b>0.88</b>	<b>0.90</b>	0.53	<b>0.85</b>	<b>1</b>						
EF(Al)Zn	<b>0.75</b>	<b>0.86</b>	<b>0.94</b>	0.55	<b>0.79</b>	<b>0.95</b>	<b>1</b>					
EF(Al)Cu	0.25	0.38	0.42	<b>0.95</b>	0.37	0.54	0.56	<b>1</b>				
IgeoAs	<b>0.74</b>	0.53	0.54	0.33	<b>0.83</b>	0.66	0.63	0.40	<b>1</b>			
IgeoPb	0.59	<b>0.74</b>	<b>0.70</b>	0.52	0.64	<b>0.81</b>	<b>0.76</b>	0.48	0.63	<b>1</b>		
IgeoZn	0.57	<b>0.77</b>	<b>0.80</b>	0.48	0.62	<b>0.82</b>	<b>0.87</b>	0.46	0.60	<b>0.80</b>	<b>1</b>	
IgeoCu	0.06	0.12	0.05	0.02	0.03	0.07	0.02	-0.07	-0.02	0.08	-0.07	<b>1</b>

Values in bold are different from 0 at significance level  $\alpha = 0.05$

Moreover, the results indicate that there is a strong and positive relationship between EF(Al) and EF(Fe) for trace metals (Pb, Zn and As), while a very weak relationship was obtained for Cu. The importance of including the correlations of EF(Al) and EF(Fe) values with the difference of the two references (Fe or Al) for the enrichment factor gave the same classification for the analyzed trace metals. This is indicated by the same results of sedimentary surface samples using EF(Al) and EF(Fe). On the other hand, Koukina and Lobus (2020) used one of the two tested references that were enriched for the same trace metals, namely Pb and Zn. The results also showed strong and positive correlations between Igeo Pb, Igeo As and Igeo Zn. These results explain the strong Igeo correlation between the three trace metals (Pb, Zn and As) and the Geoaccumulation Index, which suggests similar pollution sources. The same results of studies of sediment samples evaluating Igeo revealed that they suffer from mild to strong contamination with Zn and As (Hasan et al., 2013).

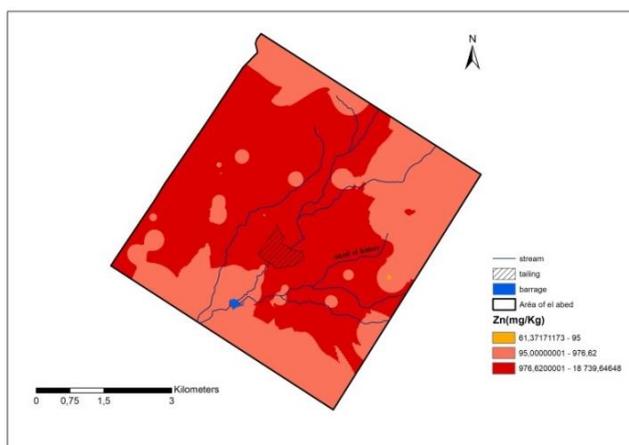
Only one negative relationship was noted between Igeo Cu and Igeo Zn ( $r = -0.03$ ). The correlation between factors and trace metals was studied. If the P value is equal to

or less than 0.05, the correlation is significant (Cohen et al., 2003; Soper, 2016). These results indicate that there is a strong relationship between the three pollution indicators (EF(Fe), EF(Al) and Igeo) for the trace elements Pb, Zn and As. These results indicate that these trace elements are from human sources. At the same time, there was a negative and weak relationship between the three pollution indicators mentioned above for Cu, which indicates its natural origin.

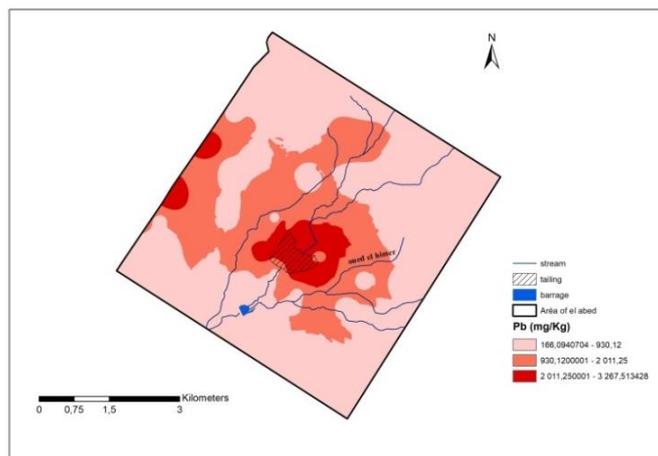
Many researchers have highlighted the role of statistics. It is an important tool for determining the factors that control trace metals in the chosen environmental media. So, these results proved that the correlation between the studied pollution factors is strong between the trace elements of surface samples (soils, sediments and mining wastes). These observations are consistent with the data and results of the study of Nikolaidis et al. (2010) on an abandoned Zn and Pb mine in northeastern Greece. The authors showed that the EF values are high for Cd, Zn and As in the surface water stream sediments as well as the agricultural fields near the mine, which were in the following order: Cd > Pb > Zn > As (Nikolaidis et al., 2010). The results of the study by Laribi et al. (2019), on the other hand, showed that the soils of the Mitidja area (Algeria) have enrichment factors for metals such as Cd, Cu, Pb and Zn, which are of human origins.

Another study on the Mitidja area showed that Cu and nickel (Ni) originate from the Earth's crust. In addition, the obtained values of the sediments Igeo were for Pb; uncontaminated to moderately contaminated, for Zn; moderately contaminated and for Cd; extremely contaminated (Laribi et al., 2017). In Beijing, Qingjie et al. (2008) have reported that the use of pollution indicators has a great role in the evaluation of the soil, so in the case of low values for all pollution indicators, the soil is reported as unpolluted.

The spatial distribution patterns of trace metals in the El Abed area were used to determine the enriched areas. Based on the geochemical maps of the trace metals, several hotspots have been identified. The spatial distribution pattern of Zn, Pb and As showed that the hotspot region is distributed over a large area of the study zone. The most important is in four directions: north, northwest, southeast as well as the center of the study region. The highest concentration of Zn (18750 mg/kg) was found northwest of the study area (Fig. 6). The distribution of Pb concentrations was similar to those of Zn and it was less prevalent and appeared in two directions: in the center of the region (Dike El Abed) and the northwest (Fig. 7).



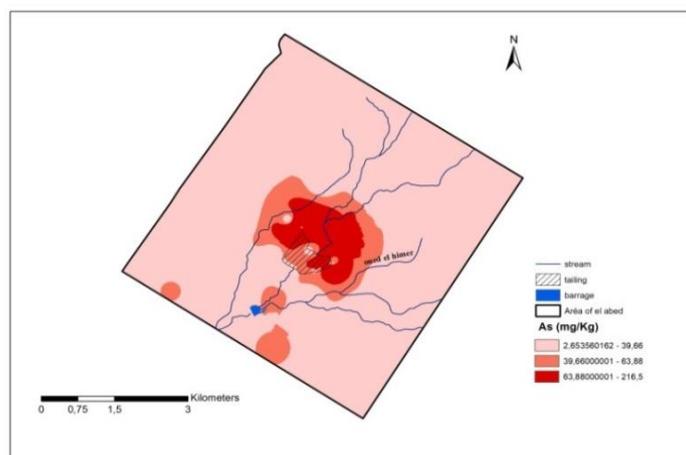
**Figure 6.** Spatial distribution map of the trace metal zinc in the soils, sediments and mining wastes of El Abed area



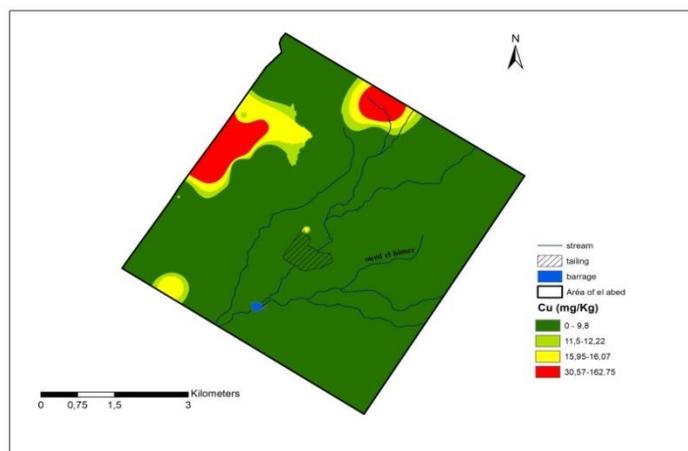
**Figure 7.** Spatial distribution map of the trace metal lead in the soils, sediments and mining wastes of El Abed area

The highest concentration of Pb (3332.5 mg/kg) was also found in the center of the study area. The highest concentration of As was found in the study center to reach the peak value of 216.50 mg/kg (Fig. 8). Du Plessis (2019) showed that the spatial distribution maps of the sediment surface samples showed the hotspots of the trace mineral Zn were in high concentrations in the Amata Pan region. In our work, the area within the field of the study showed high concentrations of Cu in the northwest (162.75 mg/kg) (Fig. 9). In the study of mining areas in the central, south and southeast of Côte d'Ivoire, the maps showed the spatial distribution of the trace metals Ni and Cu in Afena and Cd in Agbou at most points of the sites (Kinimo et al., 2018). Studies on surface soils of the European Union, using maps of trace metals concentration, have proven that Pb, Zn, Cu and As are the result of an anthropogenic effect on soil quality in Europe (Tóth et al., 2016).

The spatial distribution of metal concentrations (loid) shows that higher concentrations of As, Pb and Zn are associated with the occurrence of mine tailings because they generally have higher metal concentrations than soil/sediment.



**Figure 8.** Spatial distribution map of the trace metal arsenic in the soils, sediments and mining wastes of El Abed area



**Figure 9.** Spatial distribution map of the trace metal copper the soils, sediments and mining wastes of El Abed area

## Conclusion

This study investigated the status and sources of trace metals in selected environmental media (soils, sediments and mine wastes) around El Abed region. The concentrations of Pb, As, Cu and Zn were determined as the following order  $Zn > Pb > As > Cu$ . In addition, all metals except Cu were higher than the GBV in the Earth's crust. Based on the concentrations of trace metals Pb, As, Zn and Cu, environmental quality indicators were calculated and multivariate statistical methods were used for trace metals and pollution factors. The obtained results proved a strong relationship between the trace metals Pb, Zn and As, which indicates their human source, while for Cu, there was a weak relationship. Furthermore, the results of the spatial analysis on the basis of GIS show many hotspots in the El Abed region. These results help authorities develop strategies aimed primarily at eliminating hazardous materials from mining wastes.

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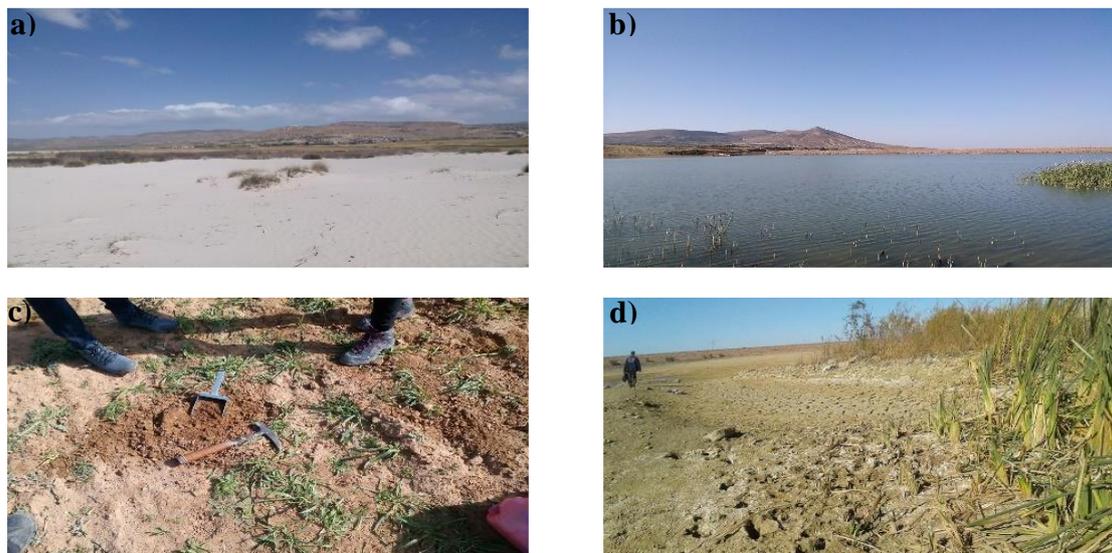
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## APPENDIX



**Figure A1.** Photos showing the the tailings dyke stored in the open area (a), the general view of the dam and the mine (b) and sampling areas (c and d)

**Table A1.** GPS coordinates of the sampling sites

Sampling site ID	Longitude 'N	Latitude 'W	Altitude
S1	62°0821.28	38°17753.21	1566
S2	62°0298.63	38°17022.08	1378
S3	62°1188.48	38°17352.84	1509
S4	62°2568.02	38°16353.28	1384
S5	62°2430.73	38°15774.7	1327
S6	62°3336.3	38°15040.75	1421
S7	62°4145.43	38°15310.02	1472
S8	62°1304.45	38°14820.22	1238
S9	62°2318.15	38°14770.65	1275
S10	62°3163.21	38°13794.96	1307
S11	62°3964.07	38°13237.76	1344
S12	61°9788.41	38°16348.14	1275
S13	62°0576.6	38°14097.5	1207
S14	62°0706.6	38°13914.3	1213
S15	62°0834.2	38°13916.1	1217
S16	61°9270.32	38°15725.9	1238
S17	62°0706.21	38°13983.34	1214
S18	62°0886.41	38°13824.24	1218
S19	62°1405.17	38°13183.99	1213
S20	62°2332.22	38°12692.39	1232
S21	62°1407.2	38°13030.1	1217
S22	62°2824.06	38°11454.14	1263
S23	61°9874.59	38°12869.59	1158

S24	62°0939.75	38°12489.32	1197
S25	62°1917.68	38°12149.31	1226
S26	61°8092.68	38°12742.97	1153
S27	61°9621.74	38°12605.69	1179
S28	62°0168.7	38°11400.37	1191
S29	62°1120.24	38°11231.55	1231
S30	62°1506.18	38°10432.13	1274
Sd1	62°0825.19	38°17746.79	1566
Sd2	62°0814.13	38°17734.01	1565
Sd3	62°0841.85	38°17701.71	1568
Sd4	62°0146.71	38°15413.68	1235
Sd5	61°9641.15	38°15262.05	1225
Sd6	61°9677.8	38°15071.19	1219
Sd7	62°1328.62	38°13182.99	1212
Sd8	62°3238.49	38°12582.03	1277
Sd9	61°9599.22	38°14475.55	1201
Sd10	62°0489.4	38°12956.4	1191
Sd11	61°8137.81	38°14213.78	1177
Sd12	61°9577.39	38°14148.99	1197
Sd13	62°0364.1	38°12769.9	1185
Sd14	61°8149.77	38°13754.1	1175
Sd15	62°0189.4	38°12459.6	1176
Sd16	62°0830.53	3812290.72	1192
Sd17	61°7708.97	3813457.51	1148
T1	62°0942.7	3813424.5	1210
T2	62°0968.5	3813394	1211
T3	61°8374.49	3814685.4	1207
T4	62°1405.97	3813122.38	1212
T5	61°8379.21	3814735.07	1208
T6	62°0235.46	3813384.15	1196
T7	62°1100.56	3813056.78	1210
T8	62°1126.48	3813026.3	1208
T9	62°1042.04	3812983.92	1207