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Spatial distribution and contamination assessment of trace metals in agricultural soils around Sidi Ahmed Pb-Zn abandoned mine, Tunisia

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ABSTRACT: The spatial distribution, source identification and contamination assessment of trace metal contents in the agricultural soils around Sidi Ahmed Pb-Zn abandoned mine, Northern Tunisia, were investigated using statistical methods, pollution indicators and geographic information system (GIS) mapping techniques. A total of 7 soil tailing samples, 54 agricultural topsoil samples and 9 background topsoil samples were collected. The concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn and Zr were then analyzed. The tailings samples are extremely rich in trace metals. The maximum concentrations in the tailings were 635.4, 618.2, 156.3, 713.8, 59989 and 91691 mg.kg^{-1} for As, Cd, Cu, Hg, Pb and Zn, respectively.

Statistical methods (descriptive statistics, Pearson's correlation coefficient analysis, principal component analysis, and cluster analysis) indicate that As, Cd, Cu, Pb, and Zn concentrations in agricultural soils around mining site are indicators of anthropogenic pollution, whereas Cr, Ni and V contents are mainly controlled by natural source in the environment.

Multivariate geostatistical analyses demonstrate that the hot-spot areas of metal contamination appeared closely to the tailings, indicating that the toxic elements could be dispersed, both downstream and downslope from the tailings, possibly due to surface run-off and strong winds. Spatial distribution of the potential ecological risk index (RI) shows that only 8.4 hectares around mining area have considerable potential ecological risk.

KEYWORDS: Trace metal, Agricultural soils, spatial distribution, Contamination assessment, Statistical methods, GIS mapping technique.

1 INTRODUCTION

Pollution of agricultural soils with trace metals due to mining activities is of great concern in northern Tunisia [1], [2]. Extraction of metals from sulfide minerals generated significant amount of waste tailings with elevated concentrations of potentially toxic metals (e.g ., Cu, Zn, Cd, and Pb) [3], [4], [5]. Most of the mining wastes were deposited in inadequate facilities or were simply released in the nearest water course. Trace elements contained in the residues from mining and metallurgical operations are often dispersed, included in particulate material or in aqueous solution by wind and/or water after their disposal [6], [7]. In semi-arid environments, such as found in northern Tunisia, the spreading of metal contamination from mining waste is often enhanced by trace winds and intense rainfall during the short rainy season [8], [9], [10], [11]. As a result large pollution of surface water, sediments and agricultural soils has taken place.

Trace metal contamination of agricultural soils surrounding the mining areas is a serious environmental problem because they have the potential to be accumulated in less soluble forms, transferred into soil solution and subsequently deteriorate the groundwater and crop quality. The food crops constitute an important source of human oral exposure to metals ([12], [13]. According to Wong [14], the monitoring of metal levels in agricultural soils is of great importance for protecting its quality and ensuring future sustainability.

The pollution indicators (Enrichment factor (EF) and geo-accumulation index (Igeo)) and the potential ecological risk index (RI) have been increasingly used to define the pollution degree of the metals and their potential ecological risk, respectively

[15], [16], [17]. Statistical methods (descriptive statistics, Pearson's correlation coefficient analysis, principal component analysis, and cluster analysis) and Geographic Information System (GIS) techniques have been increasingly used to identify contamination sources and delineate the areas at hazard of contamination [18], [19], [20], [21], [22]. In this context, the main objectives of present study were (1) to determine the concentration and distribution of trace metals in agricultural soils around the Sidi Amed Pb/Zn closed mine; (2) to identify the possible sources of trace metals; and (3) to assess the trace metal contamination in soils.

2 MATERIALS AND METHODS

2.1 STUDY AREA

Sidi Ahmed Pb/Zn mine belongs to the Nefza mining district sited in northern Tunisia. It has a humid Mediterranean climate with an annual average precipitation of 716 mm, occurring mostly during winter and autumn as trace storms. The annual average temperature is 19.9 °C, while the average minimum and maximum temperatures are 4.7 °C in February and 36.7 °C in August, respectively. The prevailing winds are from West to North West with a speed of 31 m/s.

The main flow direction of drainage systems guided by the topographic slope of the mine area is from southeast to northwest.

Sited in northern Tunisia, the study area belongs to the Nappe Zon, characterized by allochthonous thrust sheets composed by Numidian clays and sandstones, resulting from a major Neogene tectonic event [23]. Nappe pile in the study area is formed by the Kasseb and Ed Diss thrust sheets (Upper Cretaceous to Eocene) which consist of alternating marls and limestones (Fig. 1). As the entire of northern Tunisia, the soil in the vicinity of Sidi Ahmed mine is generally calcimagnesic and the dominant agricultural crops are cereals.

The Sidi Ahmed Pb–Zn mine complex consists of several mines exploited in veins [24]. The latest resulted from NNE-SSW, NW-SE and E-W faults, and locally from fillings of stratification joints. The original ore deposit mainly consists of galena, sphalerite, cerussite and smithsonite hosted in hard carbonate of lower Maastrichtian formations. Pyrite occurs as accessory mineral. The ore valorization process used, include crushing, grounding operations and flotation procedure using organic matter. The Sidi Ahmed mine was extensively exploited from 1890 until 1951 and produced over 26 200 t of Zn and 10 000 t of Pb. However, upon closure of this mine, tailings with elevated levels of toxic elements including Pb, Zn, Cd, As, Cu and Hg, were dumped along local oued without any refinement. These toxic elements have a potential to contaminate soils, sediments and water by clastic movement through wind and water.

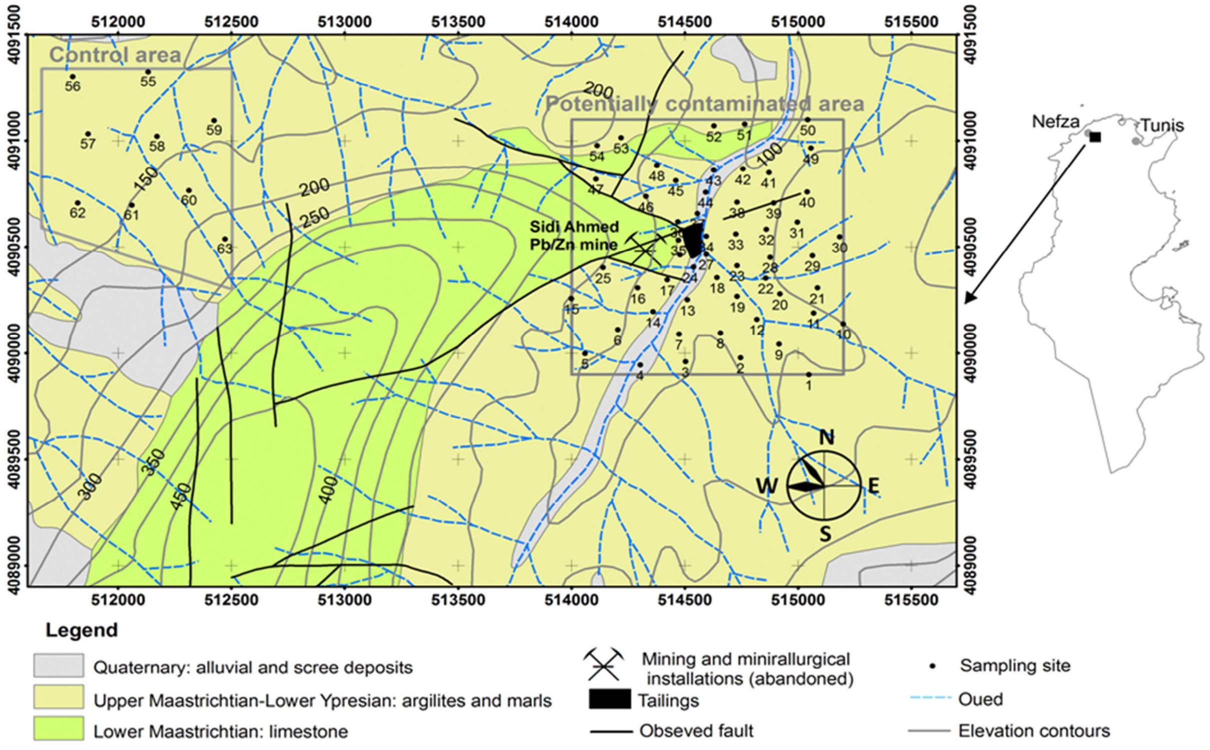

Fig. 1. Geological map (from Rouvier 1987) of Sidi Amed mining district with the position of agricultural topsoil and control samples

2.2 SAMPLING AND CHEMICAL ANALYSES

The geochemical survey was conduct in 2013 by the National Office of Mines (Tunisia). In the study area three types of samples were collected with taking into consideration the accentuated relief and the position of potential pollution sources. 7 mine waste samples were taken from mine tailings that is assumed as source of pollution, 54 agricultural topsoil samples were collected nearby the mine waste and 9 control topsoil samples were taken from the opposite site of the mine location which were assumed to represent the background concentration of investigated elements (Fig. 1). Samples from the surface soil were taken at depths of 0-20 cm. For each sampling site, three sub-samples were collected and mixed to form one composite sample using a stainless steel shovel. Geographic coordinates of the sampling points were determined using a global positioning system.

To determine trace metals concentrations, the soil and tailings samples were air-dried, sieved to <2 mm and crushed manually in an agate. Then the solid samples were digested in a triacid ($HClO_4$, HF and HNO_3) solution to determine the concentrations of Cd, Cr, Cu, Ni, Pb, V, Zn and Zr. The As and Hg contents were determined after digestion in Teflon beakers with a mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) using hot plane. Total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn and Zr in the digested solution were measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES: Ultima C of HORIBA-JOBIN YVON) at the Office National des Mines in Tunis. The limits of detection for examined metals were: 0.5 mg.kg^{-1} (As); 0.05 mg kg^{-1} (Cd); 0.5 mg kg^{-1} (Cr); 0.1 mg kg^{-1} (Cu); 0.5 mg kg^{-1} (Hg); 0.5 mg kg^{-1} (Ni); 0.5 mg kg^{-1} (Pb); 0.5 mg kg^{-1} (Zn) and 0.5 mg kg^{-1} (Zr). All analyses were taken in duplicate and mean values were adopted.

2.3 STATISTICAL ANALYSIS

Descriptive statistical parameters, involving minimum, maximum, mean, standard deviation, coefficient of variation, Skewness and Kurtosis, were implemented to characterize the distribution of trace metal contents in soil. Box-and-whisker plots were also generated for displaying the data distribution. For the box-plots, the length of the box indicates the interquartile range whereas the horizontal line within each box represents the median value.

Since principal multivariate statistical analyses are sensitive to outliers and non-normality of geochemical data sets [25], log-transformation and Box-Cox transformation [26] were performed. The Kolmogorove–Smirnov (K–S) test was used for checking data normality.

The multivariate statistical techniques through Pearson's correlation analysis, principal component analysis (PCA) and cluster analysis (CA) were applied to identify the possible sources of trace metals in the surface soils. Correlation coefficients significant at the 0.01 level are chosen for the Pearson's correlation analysis. The PCA and CA were implemented to further identify metals having similar distribution patterns. The PCA was performed with varimax rotation, in order to facilitate the interpretation of results. The CA was performed using Ward method [27] with squared Euclidean distances. The results are reported in the form of dendrogram providing a visual summary of the clustering processes. All the statistical analyses were realized using SPSS software version 20.0.

2.4 CONTAMINATION ASSESSMENT METHODS

Enrichment factor (EF), geo-accumulation index (Igeo) and potential ecological risk index (RI) were implemented to assess trace metal contamination in soil located near and surrounding the Sidi Ahmed mine. These soil contamination indicators are calculated with respect to local background. In this paper, background values were estimated from the mean concentrations of the trace metals in soil samples taken far from the mining wastes in area that has a similar lithology, soil horizons and vegetation.

Enrichment factors (EF) of trace metals were used to distinguish the anthropogenic and natural metal sources occurring and to determine the pollution degree [28], [29].

The EF of individual trace metal in the soil was calculated by equation given below:

$$EF = (C_x/C_r)/(B_x/B_r)$$

where $\mathrm{C_x}$ and $\mathrm{C_r}$ are the concentrations of the target metal and the reference metal, respectively; $\mathrm{B_x}$and $\mathrm{B_r}$ are the background concentrations of the target metal and the reference metal. In this paper, background values were estimated from the mean concentrations of the trace metals in unaffected soils of the studied area.

We select Zirconium (Zr) as a reference element, because it's relative stability on the earth and its high chemical stability during the weathering process. Generally, most of Zr minerals accumulate in placer deposits, small quantity takes part in sedimentation circulation and it absorbed by clay minerals [30]. The mean of metal concentration in the control soils were used as the geochemical background concentration of the metals. The degree of pollution deduced from the enrichment factor values was defined by Sutherland [31] (Table 1).

Geo-accumulation index (Igeo) firstly introduced by Müller [16] is equally used to evaluate the level of trace metal contamination in each sample by comparing current and pre-industrial concentrations. Geo-accumulation index is expressed by the following formula:

$$Igeo = \log_2(C_x/(k \times B_r))$$

Were $\mathrm{C_x}$ is the content of metals in examined sediment sample, $\mathrm{B_r}$ is the background content of the metal and k is the background matrix correction factor. Loska [32] proposed a factor of 1.5 for the correction of lithospheric effects and small anthropogenic influences.

Table 1 shows the seven classes of contamination level related to the geo-accumulation index, as described by Müller [16].

The potential ecological risk index (RI), presented by Hakanson [17], is used to assess the degree of HMs pollution in soil according to the toxicity of the trace metals and the response of the environment. The RI was calculated as the sum of risk factors of the trace metals, it expressed by the following equation:

$$RI = \sum_{i=1}^{n} E_i$$

Where, $\mathrm{E_i}$ is the single risk factor for trace metal i and is defined as:

$$\mathrm{E_i} = \mathrm{T_i}\frac{\mathrm{C_i}}{\mathrm{B_i}}$$

Where, T_i is the toxic-response factor for trace metal i as calculated by Hakanson [17] and Xu et al. (2008), i.e., Hg = 40, Cd = 30, As = 10, Pb = Cu = Ni = Co = 5, Cr =V= 2, Zn = 1; C_i is the measured concentration of the metal i and B_i is the background value of the metal in soils. Hakanson [17] defined four levels of ecologic risk index RI, as shown in Table 1.

Table 1. Degree of contamination by metals according to soil indices. EF-enrichment factor (Sutherland (2000); Igeo-geoaccumulation index (Müller, 1969); RI-potential ecological risk index (Hakanson, 1980).

Index	Value	Degree of contamination
EF	> 40	extremely high enrichment
	20-40	very high enrichment
	5-20	significant enrichment
	2-5	moderate enrichment
	< 2	depletion to minimal enrichment
Igeo	> 5	extremely contaminated
	4-5	strongly to extremely contaminated
	3-4	strongly contaminated
	2-3	moderately to strongly contaminated
	1-2	moderately contaminated
	0-1	uncontaminated to moderately contaminated
	< 0	Uncontaminated
RI	>600	very high ecological risk
	300-600	considerable ecological risk
	150-300	moderate ecological risk
	< 150	low ecological risk

2.5 GEOCHEMICAL MAPPING

The first step in the spatial analysis was the creation of the digital geological map of the studied area by digitalizing the 1/50000 Nefza geological map [33]. The obtained map was then overlaid with other thematic maps such as stream networks and mine waste maps. The coordinate locations of sampling soil samples, the trace metal contents and the contamination indices values were also intergraded in geo reference information system (GIS) database.

The GIS mapping technique was employed to produce the spatial distribution maps of elemental concentrations and environmental indices (EF, Igeo and RI). The inverse distance weighting (IDW) interpolator method was used for gridding the geochemical data. This technique is exact deterministic interpolator that requires very few decisions regarding model parameters as it uses distances inter sample distances only. In this study, a power and number of neighboring samples equal to 1 and 6, respectively, were chosen to clearly underline spatial variation and spatial patterns of the pollution. The ArcGIS software developed by ESRI, was used for the geochemical data gridding and mapping.

3 RESULTS AND DISCUSSION

3.1 DESCRIPTIVE STATISTICS

The descriptive statistics of the trace metal concentrations in the agricultural soils around mining site, control soil and tailings are presented in Table 2. High levels of trace metals were identified in tailing samples, with maximum contents of 635.4, 618.2, 156.3, 713.8, 59989 and 91691 mg kg^{-1} for As, Cd, Cu, Hg, Pb and Zn, respectively. These values are significantly higher than those in uncontaminated soil (He et al. 2005), and also higher than the ranges of maximum allowable concentrations (MAC), which are considered as phytotoxically excessive [34]. Thus, tailing was considered as a potentially point contamination source of trace metals in the mine area.

The mean concentrations of all traces elements in control soil samples are close to the mean of worldwide soils [35] of 5.5, 0.26, 71.9, 14.3, 42.9, 30, 92, 61, and 54 mg kg^{-1} for As, Cd, Cr, Cu, Ni, Pb, V, Zn and Zr, respectively (Table 2). All these metal contents are characterized by minimum values of coefficient of skewness and kurtosis, showing a homogeneous distribution and it is most probable that the origin of these elements isn't anthropogenic and it is predominantly lithogenic.

Therefore, the background values of the studied soils were estimated as mean concentration of As, Cd, Cr, Cu, Ni, Pb, V, Zn and Zr in control soils.

The mean concentration values of As, Cd, Cu, Pb, and Zn in agricultural topsoil samples around Sidi Ahmed mine are notable superior than their correspond concentrations found in control sol samples, while the Cr, Ni and V concentrations are comparable to their background (Table 2). The similarity of concentrations for the last elements (Cr, Ni and V) between agricultural soils samples and control samples suggests the influence of local geochemistry and regional soil characteristics, indicating natural source.

The coefficient of variation (CV) values of As, Cd, Cu, Pb, and Zn concentrations are very high indicating a significantly variation of these metal contents from site to site. Moreover, the concentrations of these elements were strongly positively skewed, with skewness values considerably higher than 1, showing the existing of some extremely high concentration values indicative of heterogeneous spatial distribution of these metal in agricultural soils.

The box plots for the concentrations of As, Cd, Cr, Cu, Ni, Pb, V, Zn and Zr are shown in Fig. 2. According to the results of Fig. 2, it is clear to see that As, Cd, Cu, Pb, and Zn have numerous outliers, which are located around mine wastes (Fig. 1). The results suggest that the elements would have a higher possibility of being influenced by anthropogenic inputs.

Table 2: Descriptive statistic of the trace metal concentrations mg kg^{-1} of tailing. control and agricultural soil samples

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**V**	**Zn**	**Zr**
Tailing samples (n=7)										
Min	368.2	409.3	68.4	100.4	478.6	25	31236	93.1	53153	52.4
Max	635.4	618.2	92.3	156.3	713.8	48.6	59989	114.4	91691	61.7
Mean	518.5	500.4	79.2	127.3	608	41.7	46137	100.8	71894	56.6
Standard deviation	86.9	72.3	9.1	19.8	84.6	7.7	11015	7.1	14171	3.2
Coefficient of variation (%)	16.8	14.5	11.5	15.6	13.9	18.5	23.8	7	20	5.7
Skewness	-0.6	0.2	0.3	0.3	-0.5	-2.0	-0.1	1.1	0.1	0
Kurtosis	0.5	0	-1.3	-0.9	-0.9	4.5	-1.8	1.2	-1.5	-1.2
Control soil samples (n=9)					< BLD[d]					
Min	3.3	0.2	62.4	11.7		36.4	26.3	74.2	49.8	51.4
Max	7.8	0.3	84.3	17.8		46.7	37.8	113.5	77.9	55.6
Mean	5.5	0.3	72	14.3		43.0	30.0	92.0	61.0	54.0
Standard deviation	1.5	0	6.8	2		3.8	3.5	10.3	9.9	1.4
Coefficient of variation (%)	27	18.7	9.5	14.2		8.7	11.7	11.2	16.2	2.5
Skewness	-0.2	-0.1	0.4	0.6		-1.0	1.4	0.6	0.8	-0.9
Kurtosis	-0.8	-1	-0.2	-0.6		-0.3	2.4	2.9	-0.6	0.3
Agricultural soil samples (n=54)					< BLD[d]					
Min	3.4	0.1	65.1	10.9		27.4	9.6	74.5	32.4	52.4
Max	24.1	3.6	84.2	53.6		51.3	716.6	105.2	1 152.9	58.3
Mean	7.9	0.6	74.7	20.3		40.8	106.5	91.4	185.7	55.1
Standard deviation	5.1	0.9	5.8	11.2		6.8	157.7	7.3	246.8	1.7
Coefficient of variation (%)	64.2	141.8	7.8	55.2		16.6	148.1	8	132.9	3.1
Skewness	1.8	2.2	-0.1	1.7		-0.5	-0.3	2.1	2.4	0.0
Kurtosis	2.2	3.8	-1.3	1.7		-1.3	-0.6	3.6	5.0	-1.3
Mean of worldwide soils[a]	9.36	0.06	20-200	20	0.03	40	10-150	90[c]	10-300	-
MACs for trace elements in agricultural soils[b]	15-20	1-5	20-200	60-150	0.5-5	20-60	20-300	150	100-300	-

[a] He et al. (2005), [b] Kabata-Pendias and Mukherjee (2007), [c] Pais and Benton Jones. 1997, [d] < BLD: below limit of detection

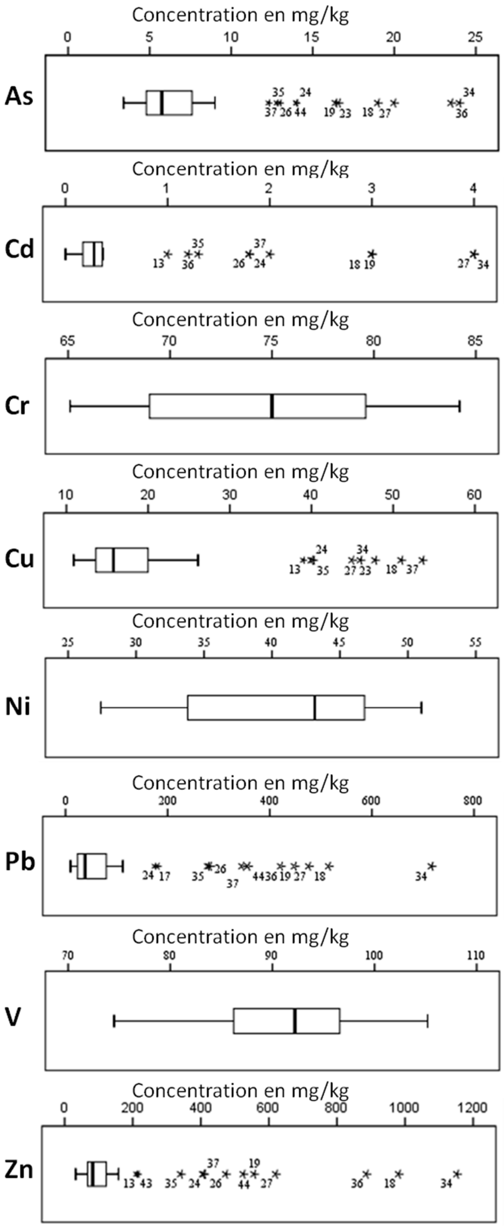

Figure 2. Box plots for the concentration of selected elements in topsoil (mg kg^{-1})

3.2 SPATIAL DISTRIBUTION

The spatial distribution of As, Cd, Cr, Cu, Ni, Pb, V, and Zn in the topsoil are represented in **Fig. 3** using contour maps based on IDW interpolator gridding. The distributions of As, Cd,

Cu, Pb and Zn, share a similar pattern (Fig. 3). The hot-spot zones of these elements are mainly associated with the mine area especially close to the mine wastes (Fig. 3). These high concentrations decreased with increasing distances from the mine waste sites. The distribution patterns observed for Cr, Ni and V were distinctly different from the trace elements discussed above (Fig. 3). The concentrations of these elements are distributed randomly and are close to, or slightly superior to their corresponding background values, reflecting a major natural lithologic source.

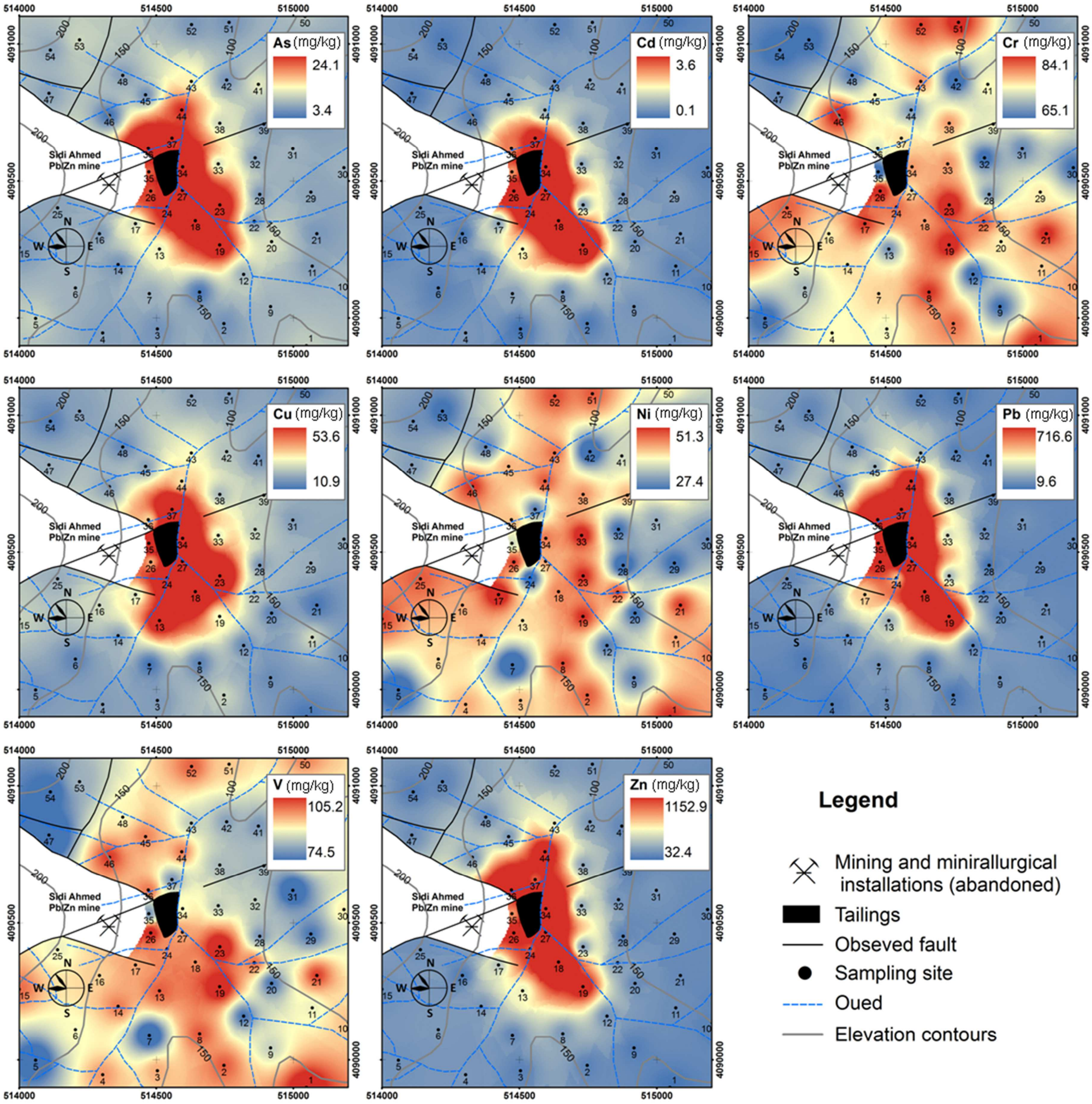

Figure 3. Spatial distribution of trace metals in the topsoil

3.3 POLLUTION ASSESSMENT

Fig. 4 shows the EF maps of As, Cd, Cr, Cu, Ni, Pb, V, and Zn. The results show that the EF values of Cr, Ni and V are less than 2 indicating deficiency to minimal enrichment levels (class 1) of these metals (Fig. 4). From the EF maps of As, Cd, Cu, Pb and Zn two different zones are distinguished. The first zone, sited close to the mining wastes, is characterized by relatively high but homogeneous EF values for As, Cd, Cu, Pb and Zn; suggest that the distribution pattern of these elements could be influenced by anthropogenic sources. The second zone, around the first one, shows low EF values for the target trace elements, reflecting weakly enrichment. The dissimilarity between the two domains can be explained by the presence of tailings. Toxic elements contained in tailings could be dispersed, both downstream and downslope from the tailings, possibly due to surface run-off and strong winds.

The geo-accumulation index maps of metals are represented in Fig. 5. From Fig. 5, it can be seen that the repartition patterns reveled by the enrichment factor maps are observed in the geo-accumulation index maps. Thus, the zones describe previously are conserved with generally same shapes and trends. The Igeo values of Cr, Ni and V are very low in the entire of study area, reflecting practically unpolluted elements. The area close to mining wastes shows the highest Igeo values of As, Cd, Cu, Pb and Zn. The remaining area exhibits low Igeo values for the target elements.

The potential ecological risk index (RI) was calculated to assess pollution by multiple trace metals in the topsoil. The spatial distribution of the potential ecological risk index in the agricultural soils is shown in **Fig. 6**. It can be seen from the map that the highest RI values were located around tailings, which was consistent with the PCA. The RI values for the remaining area were less than 300, suggesting that most areas had low to moderate ecological risk from the investigated trace metals. The polluted zone surface (8.4 hectares) of considerable potential ecological risk is relatively insignificant on comparison to the unpolluted zone surface.

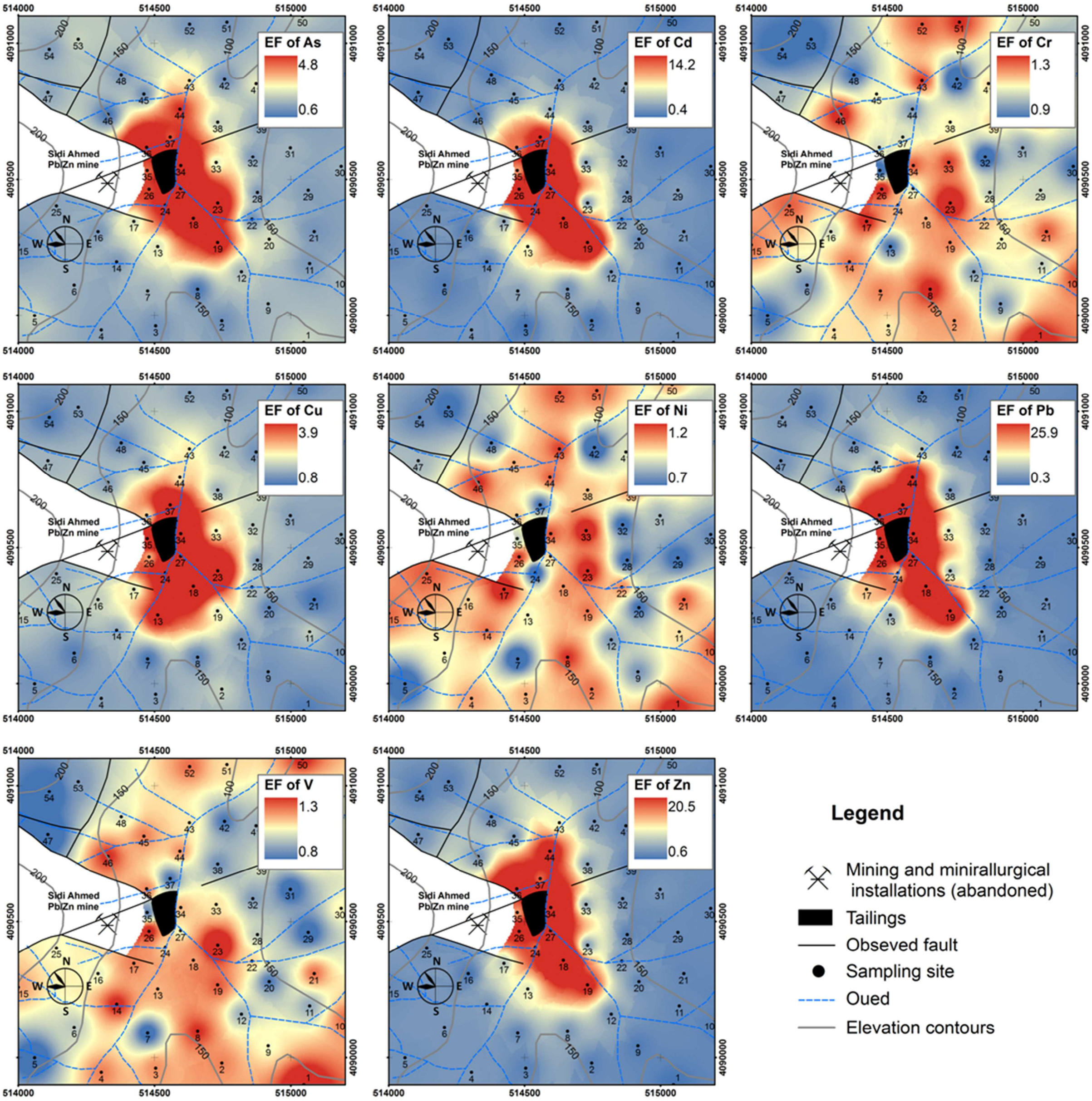

Figure 4. Spatial distribution of enrichment factor (EF) for trace metals in the topsoil

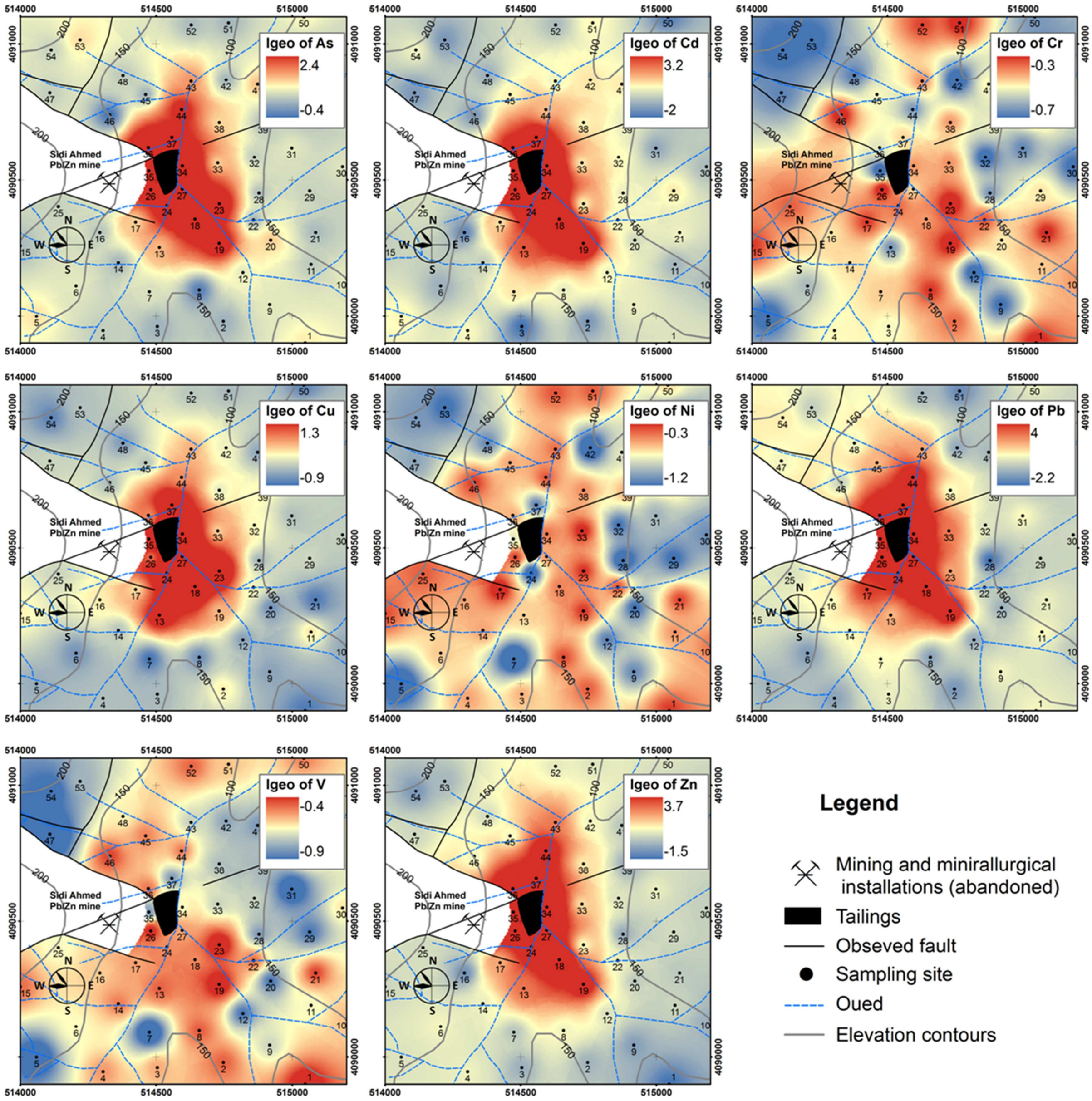

Figure 5. Spatial distribution of geo-accumulation index (Igeo) for trace metals in the topsoil

3.4 SOURCE IDENTIFICATION

To identify the possible sources of metal contamination, multivariate statistical analyses were carried out using the correlation coefficient, principal component analysis (PCA) and Hierarchical cluster analysis (HCA). The statistical distribution of raw data was checked with the test of Kolmogrov–Smirnov (K–S) for normality with a confidence interval of mean 95%. The application of the K–S test ($p > 0.05$) shows that the concentrations of Cr, Ni and V are normally distributed, while the concentrations of the rest of elements are not normally distributed (table 3). Compared with log-transformation, the Box-Cox transformation (Box and Cox 1964) has made the data more normal. Therefore, Box–Cox transformation was applied to the concentrations of As, Cd, Cu, Pb and Zn before multivariate statistical methods.

CORRELATION MATRIX

Table 4, presents the Pearson’s correlation coefficients between investigated metals. There were strong positive correlations between anthropogenic elements (As, Cd, Cu, Pb, and Zn). The strongest correlations were found between the following element concentration pairs: Cd-Zn, (r = 0.72); Cu-Zn (r = 0.71); Pb-Zn, (r = 0.69); As-Pb, (r = 0.68); As-Zn, (r = 0.68). Another strong relationship was found between Cr, Ni and V (r > 0.65).

The highly positive correlations between As, Cd, Cu, Pb, and Zn with elevated concentrations suggest that these trace metals had similar pollution levels and similar pollution sources. Moreover, the strong positive correlations between Cr, Ni and V (r > 0.65) together with relatively low concentrations, suggest that these elements are derived from parent materials.

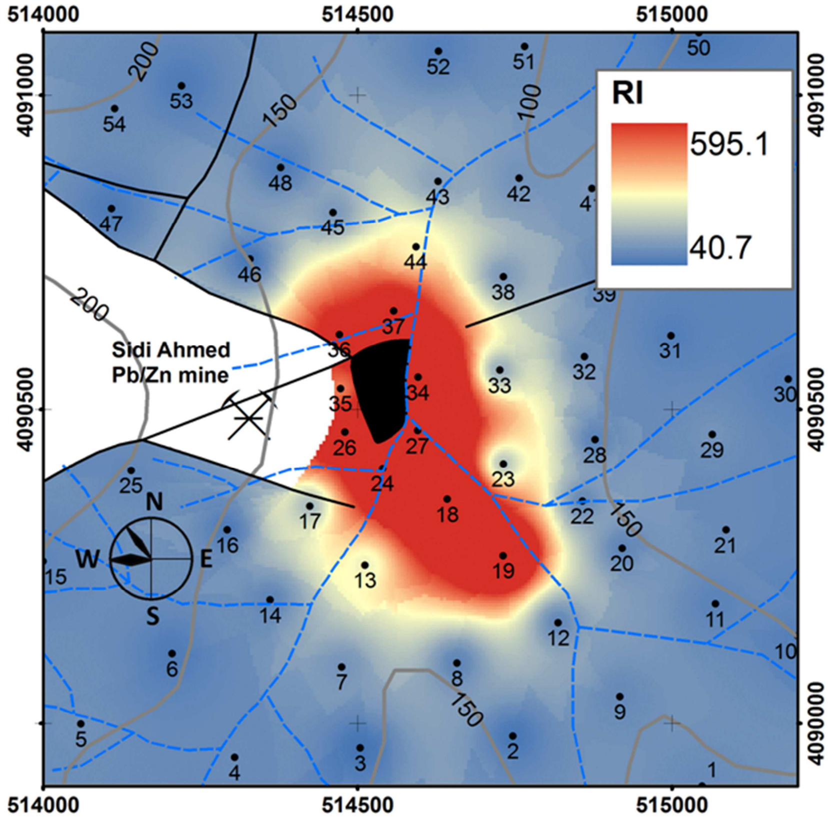

Figure 6. Spatial distribution of the potential ecological risk index (RI) for trace metals in the topsoil

Table 3. Significance level of K–S test for raw, log-transformed and Box–Cox transformed data sets

Data set	Parameter	As	Cd	Cr	Cu	Ni	Pb	V	Zn
Raw data	K-S p	0	0	0.47	0	0.06	0	0.5	0
Log-transformed	K–S p	0.01	0	0.38	0.06	0.02	0	0.49	0
Box-Cox transformed	K–S p	0.19	0.13	0.32	0.63	0.23	0.18	0.83	0.04
	Lambda	-1.3	-0.6	1.80	-1.5	2.7	-0.5	2.8	-0.7

Table 4. Pearson correlation matrix for trace metal in topsoil

	As	Cd	Cr	Cu	Ni	Pb	V
Cd	0.64						
Cr	0.30	0.14					
Cu	0.61	0.60	0.14				
Ni	0.11	0.03	0.78	0.20			
Pb	0.68	0.62	0.13	0.66	0.23		
V	0.05	0.12	0.65	0.21	0.72	0.21	
Zn	0.66	0.72	0.15	0.71	0.20	0.69	0.19

Bolded values are significant at 0.01 level

PRINCIPAL COMPONENT ANALYSIS (PCA)

Principal component analysis (PCA) was applied as a way to reduce the large number of variables to a few element associations that could be strongly correlated. Table 5 shows the factor loadings of principal components obtained by PCA using the elemental concentrations. The plot of PC loadings is shown in Fig. 7.

Two principal components with eigenvalue higher than 1, were extracted representing a total variance of approximately 76.9 %.

Table 5. Factor loadings, extraction sums of loadings and percentage of variance

Variables	F1	F2
As	0.87	-0.07
Cd	0.85	0.016
Cr	0.05	0.89
Cu	0.82	0.15
Ni	0.072	0.92
Pb	0.85	0.14
V	0.10	0.86
Zn	0.87	0.13
Eigenvalue	3.87	2.27
Variance %	46	30.9
Cumulative %	46	76.9

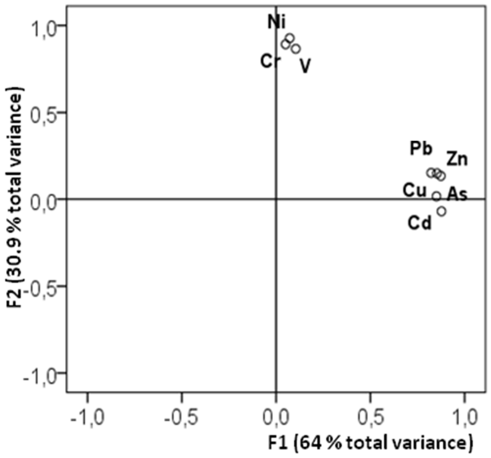

Figure 7. Factor loadings for two principal factors after varimax rotation

The first component (F1) explaining 46 % of the cumulative variance shows high loadings for As, Cd, Cu, Pb, and Zn, reflecting the anthropogenic contamination in the agricultural soils. The second component (F2) explaining 30.9 % of the cumulative variance has elevated loadings for Cr, Ni and V, reflecting the input of parent materials. The PCA is in total agreement with the elemental relationship in correlation matrix.

The spatial distribution of the two factors (F 1 and F 2) is illustrated in Fig. 8. F1 including As, Cd, Cu, Pb and Zn, shows high values in two main areas around mining wastes. The first area is more developed following NW-SE direction that coincides with the predominant NW wind direction and indicates metal dispersion from the tailings by clastic movement through wind. Tailings consisting of very fine ground barren rock with significant quantities of metals found in the host ore are very susceptible to erosion caused by wind. Wind transport of trace metal-rich particles is the important factor influencing the spreading of pollution from tailings to agricultural soils. These results were in agreement with numerous previous studies [36], [37], [38] that had found strong loadings of As, Cd, Cu, Pb, and Zn in single factor, which is interpreted as mining related anthropogenic factor. The Pb–Zn–Cu–As–Cd association is explained by the abundance of galena, sphalerite, chalcopyrite and arsenopyrite in the mining wastes due to high inefficiency of the extraction method and the concentration process of Pb/Zn ore. According to López-García et al. [39], the arsenopyrite can appear as inclusions and/or bordering the galena mineralization. Hannigton et al. [40] had shown that the Cd inclusion in the cluster could be due to the fact that this element can appear associated to sulfide minerals at concentrations greater than 0.1 wt. %. The Cr–Ni–V association may be explained by the influence of parent materials.

For F2 including V, Ni, and Cr, the high values were distributed randomly and mainly originated from the parent soil materials.

The results of Hierarchical cluster analysis (HCA) applied to trace metal contents in the soil are illustrated by a hierarchical dendrogram in **Fig. 9**. Generally, an agreement is clearly distinguished between the HCA and PCA results. Two distinct clusters are distinguished from the dendrogram. The first cluster shows high positive loading for As, Cd, Cu, Pb, and Zn, supporting anthropogenic inputs. The second cluster shows significant weights for Cr, Ni and V, suggesting the influence of natural sources.

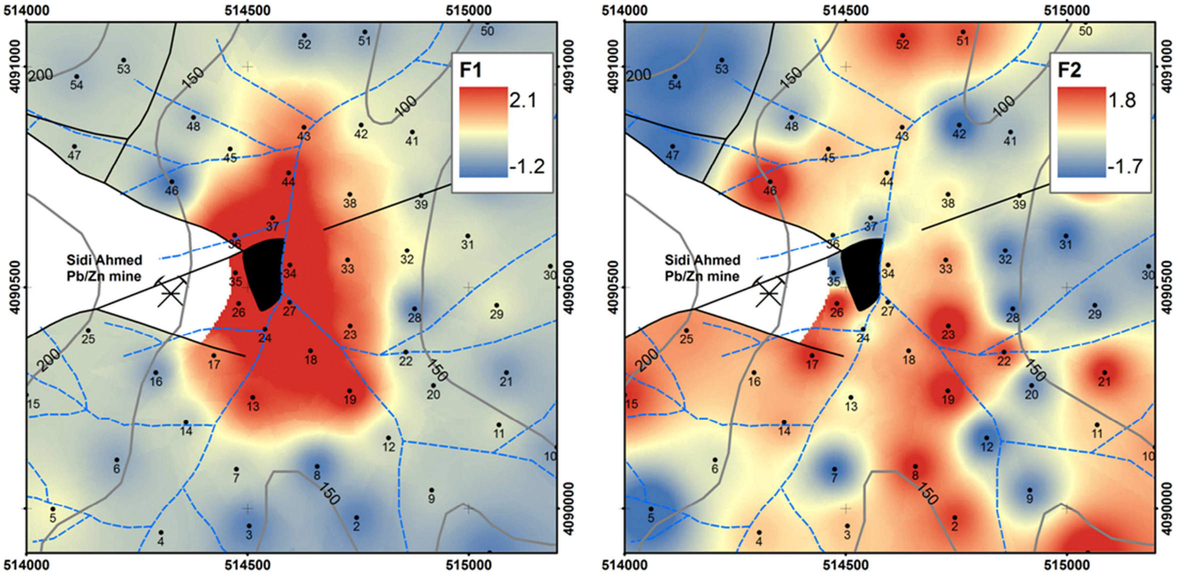

Figure 8. Spatial distribution of the factor score (F1, F2) obtained by factorial analysis

HIERARCHICAL CLUSTER ANALYSIS

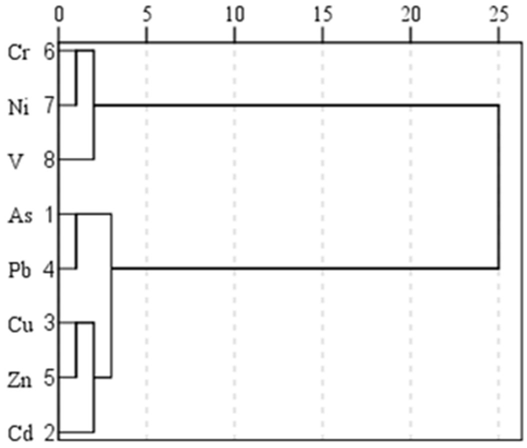

Figure 9. Hierarchical clustering of trace metals in topsoil

4 CONCLUSIONS

Statistical methods and potential ecological risk index (RI) combined with GIS mapping technique were been suggest for the assessment of extension and intensity of soil contamination with toxic elements from the abandoned Sidi Ahmed mine.

High concentrations of As, Cd, Cu, Pb and Zn were found in the tailing and the soils nearest this mining wastes. The contents of these metals decreased as far away from the mine tailing. These elements also have high EF, Igeo and RI values. Cr, Ni and V concentrations are comparable to their background, indicating natural source.

The results of descriptive statistics and multivariate geostatistical analyses in this study agree with each other confirming the presence of two clusters of metals. The first cluster contains Cr, Ni and V which mainly influenced by natural inputs. The second cluster includes As, Cd, Cu, Pb, and Zn which are related to the mining wastes. The spreading of metal pollution from tailings is enhanced by climate factors including wind and hydric transport of particles. The spatial distribution of the RI in agricultural soils shows that only 8.4 hectares of the study area have considerable potential ecological risk.

Tacking in consideration the exploitation and the unexploited periods of the Sidi Ahmed mine of 60 and 75 years, respectively, the surface polluted appear insignificant especially that is surround with agricultural domains of thousands hectares.

This paper may be a basis for future studies including temporal dimension for assessing the evolution of the polluted zone in the Sidi Ahmed site.

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REFERENCES

[1] M. Ghorbel, M. Munoz, P. Courjault-Radé, C. Destrigneville, P. De Parseval, R. Souissi, F. Souissi, A. Ben Mammou, S. Abdeljaouad, “Health risk assessment for human exposure by direct ingestion of Pb, Cd, Zn bearing dust in the former miner's village of Jebel Ressas, NE Tunisia,” *European Journal of Mineralogy*, vol. 22, no. 5, pp. 639–649, 2010.

[2] S. Boussen, M. Soubrand, H. Bril, K. Ouerfelli, S. Abdeljaouad, “ Transfer of lead, zinc and cadmium from mine tailings to wheat (Triticum aestivum) in carbonated Mediterranean (Northern Tunisia) soils,” *Geoderma*, vol. 192, pp.227–236, 2013.

[3] M. A. Othmani, F. Souissi, M. Benzaazoua, H. Bouzahzah, B. Bussiere, A. Mansouri, “The Geochemical Behaviour of Mine Tailings from the Touiref Pb–Zn District in Tunisia in Weathering Cells Leaching Tests,” *Mine Water and the Environment*, vol. 32, pp. 28–41, 2013.

[4] R. Souissi, F. Souissi, H. K. Chakroun, J. L. Bouchardon, “Mineralogical and Geochemical Characterization of Mine Tailings and Pb, Zn, and Cd Mobility in a Carbonate Setting (Northern Tunisia),” *Mine Water and the Environment*, vol. 32, pp. 16–27, 2013.

[5] G. Daldoul, R. Souissi, F. Souissi, N. Jemmali, H. K. Chakroun, “Assessment and mobility of trace metals in carbonated soils contaminated by old mine tailings in North Tunisia,” *Journal of African Earth Sciences*, vol. 110, pp. 150–159, 2015.

[6] B. G. Lottermoser, Mine wastes, Characterization, Treatment, Environmental Impacts Second ed. Springer, New York, 2007.

[7] L. Rodriguez, E. Ruiz, J. Alonso-Azcarate, J. Rincon, “Trace metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain,” *Journal of Environmental Management*, vol. 90, pp. 1106–1116, 2009.

[8] M. C. Navarro, C. Pérez-Sirvent, M. J. Martínez-Sánchez, J. Vidal, P. J. Tovar, J. Bech, “Abandoned mine sites as a source of contamination by trace metals: A case study in a semi-arid zone,” *Journal of Geochemical Exploration*, vol. 96, pp. 183–193, 2008.

[9] A. Mlayah, E. Ferrera Da Silva, F. Rocha, C. Ben Hamza, A. Charef, F. Noronha, “The Oued Mellègue: mining activity, stream sediments and dispersion of base metals in natural environments, North-western Tunisia” *Journal of Geochemical Exploration*, vol. 102, pp. 27–36, 2009

[10] R. Oyarzun, J. Lillo, J. A. Lopez-Garcia, J. M. Esbri, P. Cubas, W. Llanos, P. Higueras, “The Mazarron Pb-(Ag)-Zn mining district (SE Spain) as a source of trace metal contamination in a semiarid realm: geochemical data from mine wastes, soils, and stream sediments,” *Journal of Geochemical Exploration*, vol. 109, pp. 113–124, 2011

[11] A. El Khalil, L. Hanich, A. Bannari, L. Zouhri, O. Pourret, R. Hakkou, ”Assessment of soil contamination around an abandoned mine in a semi-arid environment using geochemistry and geostatistics: Pre-work of geochemical process modeling with numerical models,” *Journal of Geochemical Exploration*, vol. 125, pp. 117–129, 2013.

[12] Z. Cheng, L. Lee, S. Dayan, M. Grinshtein, R. Shaw, “Speciation of trace metals in garden soils: evidences from selective and sequential chemical leaching,” *Journal of Soils and Sediments*, vol. 11, pp. 628–638, (2011).

[13] P. Liu, H. Zhao, L. Wang, Z. Liu, J. Wei, Y. Wang, L. Jiang, L. Dong, Y. Zhang, “Analysis of trace metal sources for vegetable soils from Shandong Province, *China,” Agricultural Sciences in China*, vol. 10, pp. 109–119, 2011.

[14] S. C. Wong, X. D. Li, G. Zhang, S. H. Qi, Y. S. Min, “Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environmental Pollution,* Vol. 119, pp. 33–44, 2002.

[15] W. Salomons, U. Förstner, Metals in the hydrocycle. Springer, Berlin Heidelberg Tokyo, 1984.

[16] Müller, G. (1969). Index of geoaccumulation in the sediments of the Rhine River. *Geojournal*, 2, 108–118.

[17] L. Hakanson, “Ecological risk index for aquatic pollution control, a sedimentological approach,” *Water Research*, vol. 14, pp. 975–1001, 1980.

[18] E. Kelepertzis, “Accumulation of trace metals in agricultural soils of Mediterranean: Insights from Argolida basin, Peloponnese, Greece,” *Geoderma*, vol. 221–222, pp. 82–90, 2014.

[19] A. Hani, E. Pazira, “Trace metals assessment and identification of their sources in agricultural soils of Southern Tehran, Iran,” *Environmental Monitoring and Assessment*, vol. 176, pp. 677–691, 2011.

[20] C. Micó, L. Recatalá, M. Peris, J. Sánchez, “Assessing trace metal sources in agricultural soils of an European Mediterranean area by multivariate analysis,” *Chemosphere*, vol. 65, pp. 863–872, 2006.

[21] C. Micó, M. Peris, L. Recatalá, J. Sánchez, “Baseline values for trace metals in agricultural soils in an European Mediterranean region,” *Science of the Total Environment*, vol. 378, pp. 13–17, 2007.

[22] A. Facchinelli, E. Sacchi, L. Mallen, L, “Multivariate statistical and GIS-based approach to identify trace metal sources in soils,” *Environmental Pollution*, vol. 114, pp. 313–324, 2001.

[23] H. Rouvier, Carte géologique de la Tunisie, feuille n°10: Nefza. Service Géologique, Office National des Mines, Tunis, Tunisie, 1987.

[24] P. Sainfeld “Les gîtes plombo-zincifères de Tunisie, ” *Annales des Mines et de la Géologie, Tunis, Tunisie*, vol 9, pp. 1-285, 1952

[25] C. Reimann, P. Filzmoser, “Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data,” Environmental Geology, vol. 39, no. 9, pp. 1001-1014, 2000.

[26] G. E. P. Box, D. R. Cox, “An analysis of transformations,” *Journal of the Royal Statistical Society*, Series B, vol. 26, no. 2, pp. 211-252, 1964.

[27] J. Xia, Y. Y. Zhang, C. S. Zhan, A. Z. Ye, “Water quality management in China: the 23 case of the Huai river basin,” *International Journal of Water Resources 24 Development*, vol. 27, no. 1, pp. 167-180, 2011.

[28] H. Bourennane, F. Douay, T. Sterckeman, E. Villanneau, H. Ciesielski, D. King, D. Baize, “Mapping of anthropogenic trace elements inputs in agricultural topsoil fromNorthern France using enrichment factors,” *Geoderma*, vol. 157, pp. 165–174, 2010.

[29] C. Reimann, P. de Caritat, “Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry,” *Environmental Science & Technology*, vol.34, pp. 5084–5091, 2000.

[30] S. Wang, C. Zhimin, L. Dongzhao, Z. Zhichang, G. Li, “Concentration distribution and assessment of several trace metals in sediments of west-four Pearl River Estuary,”. *Environmental Geology*, vol. 55, no. 1, pp. 963–975, 2008.

[31] R. I. Sutherland, “Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii,” *Environmental Geology*, vol. 39, pp. 611–627, 2000.

[32] K. Loska, J. Cebula, J. Pelczar, D. Wiechula, J. Kwapulínski, “Use of enrichment, and contamination factors together with geoaccumulation indices to evaluate the content of Cd, Cu, and Ni in the Rybnik Water Reservoir in Poland,” *Water, Air and Soil Pollution,* vol. 93, pp. 347–365, 1997.

[33] H. Rouvier, Géologie de l'extrême Nord-Tunisien: tectoniques et paléogéographie superposées à l'extrémité orientale de la chaîne Nord-Maghrebine, Thèse Doctorat ès Science, Université de Pierre et Marie Curie, Paris, France, 1977.

[34] A. Kabata-Pendias, A. B. Mukherjee, Trace Elements from Soil to Human. Springer, New York, 2007.

[35] Z. L. He, X. E. Yanga, P. J. Stoffella, “Trace elements in agroecosystems and impacts on the environment” *Journal of Trace Elements in Medicine and Biology*, vol. 19, pp. 125–140, 2005.

[36] B. González-Corrochano, J. M. Esbrí, J. Alonso-Azcárate, A. Martínez-Coronado, V. Jurado, P. Higueras, “Environmental geochemistry of a highly polluted area: The La Union Pb–Zn mine (Castilla-La Mancha region, Spain),” *Journal of Geochemical Exploration, vol. 144, pp.345–354*, 2014.

[37] M. Anju, D. K. Banerjee, “Multivariate statistical analysis of trace metals in soils of a Pb–Zn mining area, India,” *Environmental Monitoring and Assessment*, vol. 184, pp. 4191–4206, 2012

[38] Fernandez-Caliani, J. C., Barba-Brioso, C., Gonzalez, I., & Galan, E. (2009). Trace metal pollution in soils around the abandoned mine sites of Ibrian pyrite belt (Southwest Spain). *Water, Air, and Soil Pollution*, vol. 200, pp. 211–226.

[39] J. A. López-García, C. Villaseca, L. Barbero, “Estudio preliminar de las mineralizaciones de Pb–Zn de Mazarambroz, Banda Milonítica de Toledo, ” *Boletin de la Sociedad Españ̃ola de Mineralogĭa*, vol. 26, no. A, pp. 171–172,2003.

[40] M. Hannigton, P. Herzig, S. Scott, G. Thompson, P. Rona, “Comparative mineralogy and geochemistry of gold-bearing sulfide deposits on the mid-ocean ridges,” *Marine Geology*, vol. 101, pp. 217–248, 1991.