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Assessment of Trace Elements Contamination of Agricultural Topsoil around Lakhouat Mine Area, Tunisia

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Abstract

Soil contamination by Pb, Zn and Cd was characterized in the surrounding area of the abandoned Lakhouat mine. The mine area was divided into 3 zones. Eighteen topsoil samples were sampled from each zone and were characterized, determining the total trace element concentration by acid digestion of Pb, Zn and Cd. Samples belonging to the mine tailing dam showed the highest values of contamination, with mean concentrations of 2925 mg kg^{-1} for Pb, 7297 mg kg^{-1} for Zn, and 37 mg kg^{-1} for Cd. High concentrations of Pb, Zn and Cd were found in many samples taken from the surrounding soils and agricultural soils, indicating the extent of spreading pollution of trace elements. Contaminations in soils were classified as enrichment factor, contamination factor and contamination degree. Factor values indicate that trace elements contamination levels of soils on the 3 studied zones are classified as high contamination factors. A principal component analysis revealed the presence of one common source in the mining area. Cluster analysis showed a close association between soils with similar trace elements concentration. Spreading of tailing wastes from dams of the mining facilitating via rain or wind is the main source of soil contamination of agricultural soils.

Keywords: Trace elements, contamination, Lakhouat mine, mine tailings, contamination factors

Introduction

The study of trace elements contamination is of increasing interest because of the awareness that trace elements present in soils may have negative consequences on human health and on the environment [1-5]. The most important impact of soil contamination on environmental is that contaminants in soil can be introduced into the food chain by plants and by their consumption by animals [6]. Trace elements taken into the human body at doses higher than the limit values proposed by the World Health Organization (WHO) are known to cause certain types of cancers and cardiovascular diseases [6]. Therefore, trace elements pollution in areas of agricultural activities is of great concern.

Recently, there is a growing concern towards the environmental effects of mining tailing sites [7-10]. Tailings are produced during ore processing and are characterized by high concentrations of trace elements. Exposure of tailings dams to air, oxidation and climatic conditions favor the release of trace elements [9,11]. Hydric transport, wind transport and leaching processes are major factors which contribute to the trace elements in the environment and cause contamination of the surface water, groundwater and soil, which can pose serious geochemical risks to human health and the environment [9,12,13]. This hazard is aggravated by the long-term persistence of trace elements in the environment.

Agricultural soils in areas surrounding mines can be contaminated by these trace elements as well as the major ore metals [9,14]. It has been shown that distance from the source, the direction of winds, the soil physicochemical properties and interception by the environment may influence agricultural soil surrounding mine area [15].

Comprehensive methods for identifying and assessing severity of soil contamination by trace elements have been introduced in the past few decades [16,17]. One approach to characterizing pollution signals is to compare element concentrations and establish guidelines for the environmental media. Furthermore, several other methods for determining the extent of pollution in soils have been established by various authors in many parts of the world [16,18,19]. A common approach to estimate how much the soil is affected with trace elements is to evaluate the enrichment factor (EF), contamination factor (C_f) and contamination degree (C_{deg}) for element concentrations above uncontaminated background or reference levels [20]. Soil contamination by trace elements will be measured as the amount of sample element enrichment and sample element concentration above the concentrations present in the reference material [19].

The objectives of this study were to (i) analyze the total concentration of Pb, Zn and Cd in topsoils at the Lakhouat mine, (ii) carry out a preliminary assessment of the environmental risk associated with trace element pollution in soils by calculating contamination indexes and (iii) classifying soils following the trace elements concentrations by multivariate analysis.

Material and methods

Study area and soil sampling

The Lakhouat mine is located in West-Northern Tunisia (UTM Zone 32 North 522005.378/ 4014334.773) (**Figure 1**) is characterized by a sub-humid to semi-arid climate. The heavy rainy season occurs from September to April. The most rainfall occurs in January with 64.9 mm and the driest month is July with 2.5 mm. The highest temperature was recorded in July with 29.2 °C and lowest was recorded in January at 10.4 °C [21]. The monthly average humidity ranges from 69 % in January to 41.5 % in July. The prevalent winds in Lakhouat mine are from the north-east to the south-west and have an average speed of 2.85 m/s. In the Lakhouat mine, ore deposits contained galena, sphalerite, pyrite, marcasite and calcite. The tailings from the Lakhouat mine are stored in 3 dams (**Figure 1**). The adjacent areas are cultivated lands with various annual crops, essentially cereal. The mine was closed in 1992 due to the depletion of reserves.

The location of the sampling points is shown in **Figure 1**. To investigate the impact of distance on trace elements distribution and trace elements scattering to agricultural soils, the study area was divided into 3 zones from the trace element source (Tailing Dam 1) to agricultural soils plots (**Figure 1**). Zone 1, located at the mining area, acts as contaminant source of soluble and particulate trace elements from tailing Dam 1 (Samples S1, S2, S3, S4, S5 and S6). Zone 2, located in the surroundings of mining area, was selected as an example of an area which can receive the soluble and particulate trace elements (Samples S7, S8, S9, S10, S11 and S12) and Zone 3 represented the agricultural soils (Samples S13, S14, S15, S16, S17 and S18). A total of 18 samples were collected from within each zone from 0 to 30 cm depth (**Figure 1**), to be representative of the different contaminated soils. The samples were placed in polyethylene bags for transport to the laboratory. Next, the samples were air-dried at ambient temperature for 72 h, disaggregated and sieved through 2 mm. The main physicochemical properties of the soil samples were determined.

Soil analysis

The main physicochemical properties of the soil samples were characterized by the following methods: pH in H_2O using a pH meter in 1:2.5 distilled water to soil extracts [22]; Electrical conductivity (EC) was also determined according to the U.S. Salinity Laboratory Staff [23]. Texture was determined following the pipette method described by Kroetsch and Wang [24]. The effective cation exchange capacity (CEC) of the soil and exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES) (Optima 4300 DV, Perkin-Elmer, Germany) after extraction with 0.1 mol L^{-1} $BaCl_2$ [25].

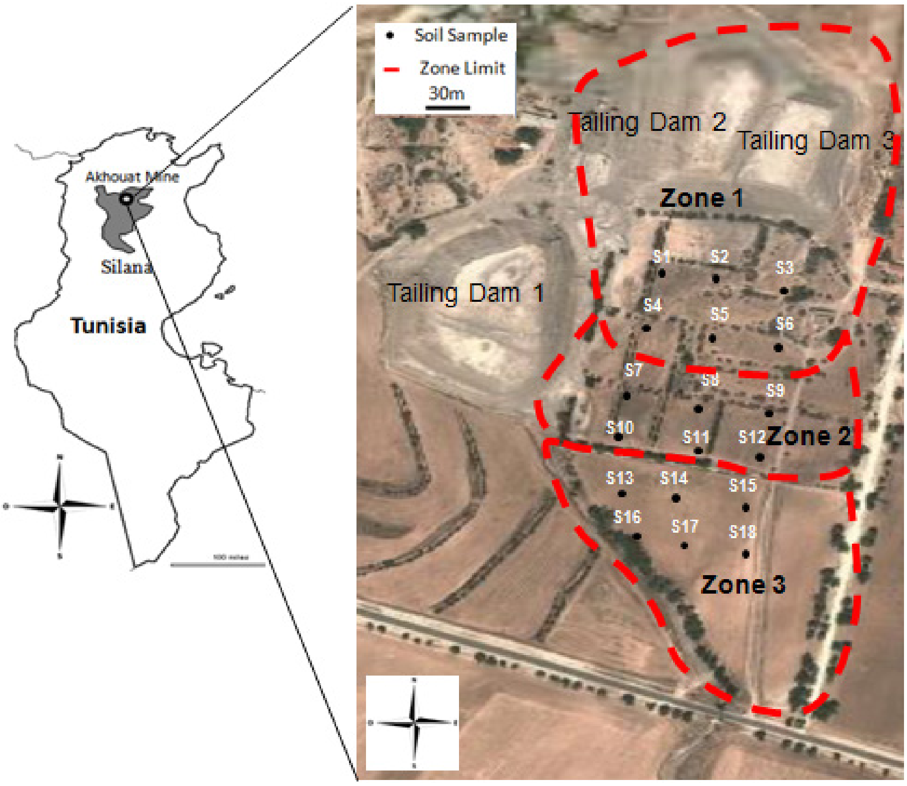

Figure 1 Location of sampling areas at the Lakhouat Mine (Google maps: https://maps.google.com).

Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide, the upper fraction (down to 50 mm) being separated by sieving and the lower one used for analysis using the internationally endorsed procedure [24]. Organic matter (OM) content was determined by soil oxidation with potassium dichromate ($K_2Cr_2O_2$) and concentrated H_2SO_4 [26]. Total Kjeldahl-N (organic plus ammonium-N) was determined according to Bremmer and Mulvaney [27]. The P content was extracted using the Mehlich-3 method [28]. The carbonate content was determined with a LECO-100 analyzer connected to a LECO- CN-2000.

To determine the total concentration of Pb, Zn and Cd in the soil samples, 1 g of sample was digested with a mixture of acids (9 ml of concentrated HNO_3 + 3 ml of concentrated HCl) in a hot plate according to method of Marcet *et al.* [29]. After digestion, the trace elements concentration was measured by ICP-OES (Perkin Elmer Optima 4300DV. All the samples were analyzed in triplicate.

Enrichment factor, contamination factor and contamination degree

In the determination of enrichment factor, soil contamination and contamination degree are used. Enrichment factors were calculated using titanium as the reference element and the pedogeochemical background Earth's Crust in the classic formula shown below [30]. Enrichment factor (EF) is divided into 5 groups [31] (**Table 1**).

$$EF = (C_n/C_{Ti})_{sample}/\ (C_n/C_{Ti})_{pedogeochemical\ background} \quad (1)$$

C_n: element concentration; C_{Ti}: Titanium concentration.

In the present study, the modified form of the method suggested by Loska *et al.* [32] for calculation of contamination factor by Hakanson [19] was used. Hakanson [19] divided the contamination factor into 4 groups (**Table 2**). The contamination factor is computed from the following equation;

$$C_f = C_o / C_n \tag{2}$$

where C_o is the mean content of trace elements of at least 5 sampling areas, C_n is the concentration of elements in the Earth's crust.

The contamination factor reveals contamination of only one element. The sum of the contamination factors of all the elements yields the contamination degree (C_{deg}) of the contaminated area. The contamination degree is divided into 4 groups as described by Hakanson [19] (**Table 3**).

Table 1 Enrichment factor (EF) classification.

EF < 2	Deficiency to minimal enrichment
EF = 2 – 5	Moderate enrichment
EF = 5 – 20	Significant enrichment
EF = 20 – 40	Very high enrichment
EF > 40	Extremely high enrichment

Table 2 Contamination factor (C_f) classification.

$C_f < 1$	Low contamination factor indicating low contamination
$1 \leq C_f < 3$	Moderate contamination factor
$3 \leq C_f < 6$	Considerable contamination factor
$6 \geq C_f$	Very high contamination factor

Table 3 Contamination degree (C_{deg}) classification.

$C_{deg} < 8$	Low degree of contamination
$8 \leq C_{deg} < 16$	Moderate degree of contamination
$16 \leq C_{deg} < 32$	Considerable degree of contamination
$32 \geq C_{deg}$	Very high degree of contamination

Statistical analysis

All statistical analysis was carried out using the software SPSS® for Windows version 20.0. Pearson's correlation coefficient was used to measure the degree of relationship between the physicochemical properties and total trace elements concentrations.

Statistical significance of differences was determined by using one-way analysis of variance (ANOVA). The data set for trace elements concentrations was subjected to principal component analysis (PCA) in order to highlight the relations between the analyzed elements. Cluster analysis (CA) was applied to group the samples with similar trace elements content. CA was undertaken according to the Ward-algorithmic method. Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters (squared Euclidean distance) are represented.

Results and discussion

Soil characterization

General soil characteristics of the Lakhouat mine area are presented in **Table 4**. The pH was alkaline (8.15, 8.26 and 8.50 in Zone 1, Zone 2 and Zone 3, respectively). The alkalinity of the soils could be attributed to the presence of carbonates in soil samples.

Most of the soils are moderately saline with an electrical conductivity (EC) in the saturation paste extract below 1 dS m^{-1}. In spite of these low values, salinity could facilitate the mobility of some trace elements especially Cd [35]. This issue has been tackled in other studies on soils with similar conditions [36]. The particle size distribution of soils exhibits a substantial variation in sand, silt, and clay contents, from a sandy texture in Zone 1 to a clay texture in Zones 2 and 3. Effective cation exchange capacity (CEC) showed a little broad interval of variation from between zones (17.27 cmol kg^{-1}, 29.36 cmol kg^{-1} and 29.37 cmol kg^{-1} in Zone 1, Zone 2 and Zone 3, respectively).

The presence of a vegetation cover near tailing dam and in some parts of the mining area could explain the moderate values of organic matter (OM) content in soils samples corresponding to Zone 1. In addition, N content exhibited a steady increase, with 0.31, 0.77 and 0.89 % for Zones 1, 2 and 3, respectively. This fact was related to the land plants covering, which presented a poor spontaneous species in Zone 1 and cereal crops in Zones 2 and 3. The percentages of carbonates are low in Zone 1 (8 %) and presented a moderate content in Zone 2 (15 %) and Zone 3 (27 %).

The levels of OM, high percentages of clay and the presence of carbonate in Zones 2 and 3 seem to suggest an important retention of trace elements by these components [37-40]. According to these results, the bioavailability and mobility of trace elements would be expected to be low in the studied soils [7].

The basic descriptive statistics for each zone and the results of one-way ANOVA for comparison of the average trace elements concentrations in soil between these zones are presented in **Table 5**.

The trace elements concentrations in all samples exceed reference values reported by Kabata-Pendias and Pendias [41] for agricultural soils with a pH > 7 (**Table 5**). In addition, several patterns of change of trace element concentrations were detected. In fact, significant differences between the zones were observed for concentrations of Pb, Zn and Cd. This is in accordance with findings of similar studies worldwide that trace element-particles can be found far away from the mining area, even in a non-prominent wind direction [10,42].

Furthermore, Zone 1 has high trace element concentrations average with 2925, 7297 and 37 mg kg^{-1} for Pb, Zn and Cd, respectively. The highest trace element concentrations were also detected in Zone 1 with 3958, 8733 and 39 mg kg^{-1} for Pb, Zn and Cd, respectively. This may be explained by the presence of the Dam 1 in Zone 1 (**Figure 1**), which represents the main source of soil contamination by trace elements.

Many researches on soil contamination by trace elements near the mining area worldwide found that the average concentrations of Pb, Zn and Cd in the surrounding soils were above the natural soil background levels. In addition, trace element concentrations were within the range of those of other mining sites in Tunisia, including the Bougrine, Boujaber, Slata and Fedj Lehdoum [10]. Furthermore, about 4-fold higher Pb, Zn and Cd concentrations were reported by Bech *et al.* [43] for soils in the surroundings lead mining in Bellmunt (Spain) and were several-fold lower than those reported by Navarro *et al.* [44] and Iavazzo *et al.* [45,46].

Taking into account the high trace elements concentration on the study area, we recommended a revegetation work using hyperaccumulating species of Pb, Zn and Cd, such as *Atriplex purpurea* and Paulownia tomentosa, and thus, avoiding problems of toxicity [47,48].

Table 4 Physicochemical characteristics of the mine soils in the sampling areas Zone 1, Zone 2 and Zone 3.

Soil characteristic	Zone 1	Zone 2	Zone 3
pH (H_2O)	8.15c $^{a)}$	8.26b	8.50a
EC (dS m^{-1})	1.07a	0.24b	0.23b
Sand (%)	45a	3c	15b
Silt (%)	7c	8b	22a
Clay (%)	48c	89a	63b
CEC (cmol kg^{-1})	17.27b	29.36a	29.37a
OM (%)	1.69a	1.62a	1.42b
Carbonate contents (%)	8c	15b	27a
N(%)	0.31b	0.77a	0.89a
P (mg kg^{-1})	13.72c	27.08a	20.44b

a) Means followed by the same letter(s) within each row are not significantly different at $P < 0.05$ (n = 3).
c) Not detectable.

Table 5 Basic statistical parameters of trace elements concentrations in soils at the Lakhouat mine (data in mg kg^{-1}).

		Pb	Zn	Cd
Zone1	Maximum	3958a	8733a	39.1a
	Minimum	2165a	5634a	36.2a
	Median	2549a	7629a	37.05a
	Average	2925a	7297a	37.33a
Zone1	Maximum	1852b	5624b	36b
	Minimum	1107b	4256b	22.8b
	Median	1420b	4966.5b	28.4b
	Average	1447b	4935b	29b
Zone1	Maximum	1065c	4220c	21.3c
	Minimum	198.7c	840c	7.2c
	Median	692.5c	2141c	13.5c
	Average	690c	2327c	14.03c

Means followed by the same letter(s) within each column for each zone are not significantly different at $P < 0.05$ (n = 3).

Correlation analysis

Pearson correlation analysis between concentrations of different trace elements in soil samples and physicochemical properties are shown in **Table 6**. OM and pH showed a positive linear relationship with all the elements analyzed despite the fact that OM content was low in the study area (**Table 3**). EC only showed a positive relationship with Cd content. Doner [35] found that the substitution of sodium in the exchange positions can produce desorption of Cd. This result may suggest a higher bioavailability of Cd in some soils with salinity problems.

Trace elements are generally closely associated with each other. **Table 2** shows that all elements are significant at a level of $P < 0.05$. Significant and high correlations between these elements indicate that contaminants and hazardous trace elements in the Lakhouat mine soils have a similar source which originates from abandoned tailing dams.

Table 6 Correlation between trace element concentrations and studied soil properties.

	pH	**EC**	**OM**	**Clay**	**Silt**	**Sand**	**Carbonate**	**Pb**	**Zn**	**Cd**
pH	1									
EC	-0.879(**)	1								
OM	0.959(**)	-0.067	1							
Clay	-0.282	0.183	-0.177	1						
Silt	-0.813(**)	-0.531(*)	-0.918(**)	-0.094	1					
Sand	0.585(*)	0.031	0.526(*)	-0.923(**)	-0.298	1				
Carbonate	-0.884(**)	-0.464	-0.955(**)	0.217	0.951(**)	-0.577(*)	1			
Pb	0.951(**)	0.188	0.894(**)	-0.471(*)	-0.714(**)	0.729(**)	-0.846(**)	1		
Zn	0.941(**)	0.011	0.941(**)	-0.292	-0.791(**)	0.587(*)	-0.866(**)	0.933(**)	1	
Cd	0.941(**)	0 .652(**)	0.959(**)	-0.190	-0.849(**)	0.512(*)	-0.891(**)	0.858(**)	0.938(**)	1

*Correlation is significant at $P \leq 0.05$
**Correlation is significant at $P \leq 0.01$

Assessment of soil contamination in Lakhouat mine

In order to determine the general contamination in the 3 studied zones of Lakhouat mine, the enrichment factor (EF), the contamination factor (C_f) and contamination degree (C_{deg}) was used. Contamination factor and contamination degree values computed for each element are provided in **Table 7**. The elements in each zone were classified on the basis of the contamination factor calculations. Accordingly, the 3 zones presented very high contamination factors. The lowest C_f values were recorded on agricultural soils (Zone 3), with C_f value 13 for both Pb and Zn, and 72 for Cd which point to very high contamination factors.

The sum of the contamination factors determined for each element yields the contamination degree. The contamination degree for the 3 zones soils is found to be 683, 462 and 223 for Zone 1, Zone 2 and Zone 3 respectively, which is noticeably higher compared to the classification proposed by Hakanson [19]. The contributions of each element to the contamination degree in the 3 zones are 50 % by Pb, 34 % by Zn and 16 % by Cd.

The EF for Pb and Zn presented extremely high enrichment values on Zone 1 and Zone 2, whereas on Zone 3 the minimum values point to significant enrichment, while maximum values imply extremely high enrichment of soils. The minimal EF average for Cd was recorded in Zone 3 with 140, which points to extremely high enrichment with Cd.

Principal component analysis (PCA) and cluster analysis (CA)

The PCA based results for soil heavy metals are listed in **Table 8**. According to the initial eigenvalues, only one principal component is selected, accounting for over 98.16 % of the total variance. The eigenvalues of the extracted component are greater than the ones before and after the matrix rotation. All of the trace elements are consequently grouped into a one component model indicating that the 3 studied trace elements are associated and have one common source in the mining area, thus showing high values in the principal component which explains 98.16 % of the total variance and loads heavily on Pb (0.998), Zn (0.952), and Cd (0.934).

The cluster analysis Ward's method and squared Euclidian distance are used to amalgamate the elements. In this study, CA is developed on soil samples, in order to identify similarities in trace element concentrations between the analyzed soil samples. The results are shown as a dendrogram, where the distance axis represents the degree of association between groups of variables, i.e. the lower the value on the axis, the more significant the association (**Figure 2**).

Two main clusters are distinguished:

- Cluster 1 groups soils S1, S2, S3 and S4 i.e. soils near the tailing Dam1, the main source of contamination by trace elements.

- Cluster 2 contains 3 subclusters. The first group soils S5, S6 and S7 situated on the limit of Zone 1 and Zone 2; the second group soils S9 to S15 situated on the limit of Zone 2 and Zone 3 and the third concerns S16, S17 and S18 located in Zone 3 with the lowest trace elements concentrations.

Table 7 Enrichment factor (EF) Contamination factor (C_f) and Contamination degree (C_{deg}) on Zone 1, Zone 2 and Zone 3.

		Enrichment factor (EF)			**Contamination factor (C_f)**			**Contamination degree (C_{deg})**
		Pb	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	
Zone 1	Average	198	112	373	198	112	373	683
	Maximum	267	134	391	267	134	391	793
	Minimum	146	87	362	146	87	362	595
	Median	172	117	371	172	117	371	660
Zone 2	Average	98	76	288	98	76	288	462
	Maximum	125	87	360	125	87	360	572
	Minimum	75	65	228	75	65	228	368
	Median	96	76	284	96	76	284	456
Zone 3	Average	47	36	140	47	36	140	223
	Maximum	72	65	213	72	65	213	350
	Minimum	13	13	72	13	13	72	98
	Median	47	33	135	47	33	135	215

Table 8 Total variance explained and component matrixes for trace elements concentration (one-components extracted).

Component	**Initial Eigenvalues**			**Extraction Sums of Squared Loadings**			**Component**	
	Total	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**		
1	6742169.766	98.164	98.164	2.774	92.479	92.479	Zn	0.998
2	126061.651	1.835	100.000				Pb	0.952
3	14.622	0.000	100.000				Cd	0.934

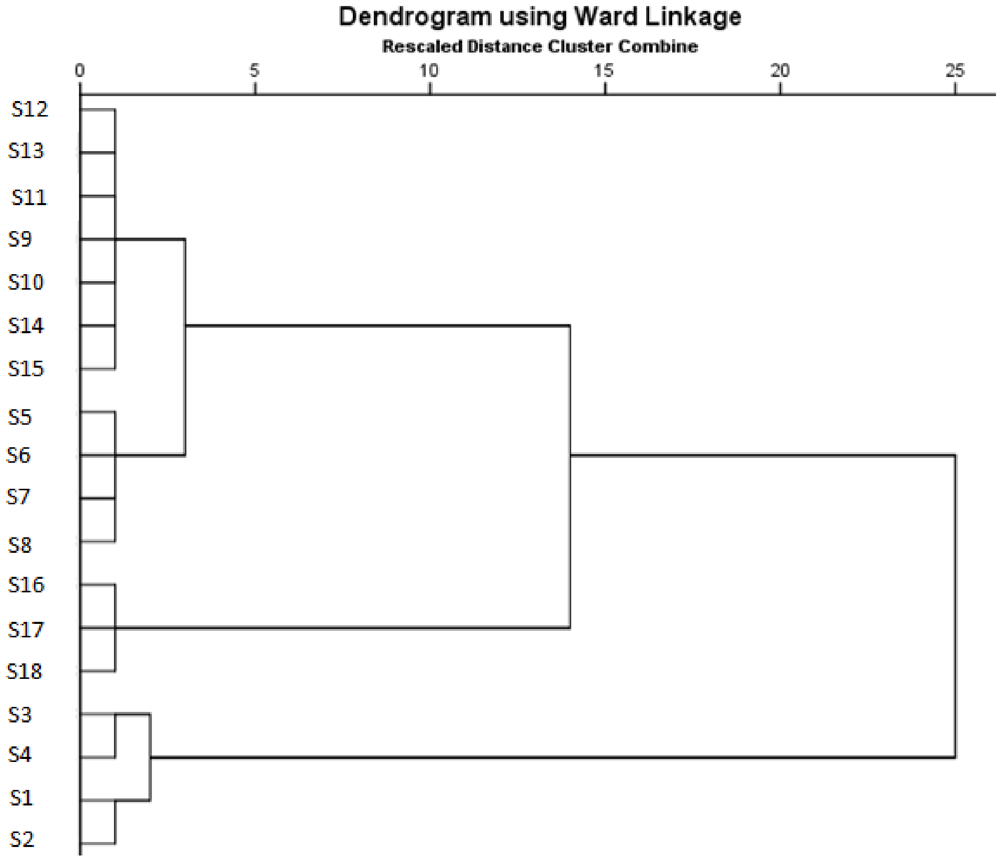

Figure 2 Dendrogram obtained by cluster analysis for soil samples.

Conclusions

This paper aimed to investigate the impact of mining on the trace elements contamination of soils belonging to both mine tailings dam and the surrounding agricultural plots. High concentrations of trace elements were detected in the entire mine area and surrounding zones, with almost all the samples exceeding the maximum tolerable concentrations for Pb, Zn and Cd established by most directives for the agricultural soils. As regards to the surrounding zones, moderately high concentrations of Pb, Zn and Cd were detected in many of the samples, showing a certain extent of dispersion of pollution from the mine area. According the trace elements concentrations, 3 zones were distinguished. Contaminated soils on these zones suggested that water and wind transport of tailings from the dam were the main effects causing the dispersion of pollution. In addition, a high enrichment factor, contamination factor and contamination degree were founded in the soils of Zone 1, Zone 2 and Zone 3. Moreover, a high significant correlation obtained between all the trace elements analyzed in the soil samples strongly suggested their common origin in mining activities.

Based on environmental health criteria, 2 measures must be done at Lakhouat mine and also for the similar mines. As an immediate measure, which is a short-term measure a barricade should be proposed to cover the abandoned mine and the surrounding agricultural area, thus creating a protection of the mine area. In the contaminated area, any agriculture activities must be forbidden. Further, soil remediation must use remediation techniques such as phytoremediation to mitigate pollution.

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