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HEAVY METALS DISTRIBUTION AND MOBILITY IN FLOTATION TAILINGS AND AGRICULTURAL SOILS NEAR THE ABANDONED Pb-Zn DISTRICT OF JEBEL HALLOUF-SIDI BOUAOUANE (NW TUNISIA)

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Abstract: Mineralogical and geochemical analyses of the environmental components in the vicinity of the abandoned mines of Jebel Hallouf-Sidi Bouaouane have shown that large volumes of flotation tailings are made of base metal sufides (galena, sphalerite, pyrite, marcasite) accompanied with lesser amounts of sulfosalts (jordanite, tennantite) and associated to a carbonated (calcite) and clayey (kaolinite, illite) matrix. Strong heavy metals (Pb, Zn and Cd) concentrations are recorded in soil and flotation tailings. Their concentrations in the flotation tailings are around 9250 $mg \cdot kg^{-1}$, 8200 $mg \cdot kg^{-1}$ and 66.5 $mg \cdot kg^{-1}$, respectively. Their mean concentrations in the soils surrounding the aforementioned mine wastes, are 39,720 $mg \cdot kg^{-1}$, 9030 $mg \cdot kg^{-1}$ and 86 $mg \cdot kg^{-1}$, respectively. Erosion by wind and running waters (heavy rain and flood periods) are considered as important mechanism in carrying these toxic elements to flood areas, and especially to soils lying on the eastern side of Jebel Hallouf Mountain. The statistical analyses of geochemical data relative to mine wastes and soils display a relationship between heavy metals and clay. Another relation is established between these metals and iron oxides. In soil, the multivariate statistical approach [principal component analysis (PCA)] has shown two contamination origins: the mining wastes and rock dumps (F1xF2 diagram). Heavy metals concentrations in batch solutions of the contaminated soil samples varied between 36.6 $\mu g \cdot l^{-1}$ and 51.2 $\mu g \cdot l^{-1}$ for Pb, 543 $\mu g \cdot l^{-1}$ and 3600 $\mu g \cdot l^{-1}$ for Zn and 0.2 $\mu g \cdot l^{-1}$ and 2.5 $\mu g \cdot l^{-1}$ for Cd, while for the flotation tailings the concentrations varied between 16.9 $\mu g \cdot l^{-1}$ and 483 $\mu g \cdot l^{-1}$, 63 $\mu g \cdot l^{-1}$ and 3240 $\mu g \cdot l^{-1}$, and 2 $\mu g \cdot l^{-1}$ and 9.8 $\mu g \cdot l^{-1}$ for the same elements respectively. Concentrations of the same order are measured in meteoric water samples taken at the top of the flotation tailing piles essentially for Zn (145 $\mu g \cdot l^{-1}$ to 1933 $\mu g \cdot l^{-1}$) and Cd (4.6 $\mu g \cdot l^{-1}$ to 34.6 $\mu g \cdot l^{-1}$). These results express the high mobility of heavy metals as to exceed the environmental norms especially for Pb in the contaminated soils as well as Pb and Cd in the flotation tailings leaching solutions.

Keywords: Heavy metals, abandoned mine, calcareous soil, horizontal dispersion, PCA, batch testing.

1. INTRODUCTION

The mining activity in Tunisia was particularly developed during the 20th century (1891-1986) for the extraction of lead (galena, PbS), zinc (sphalerite, ZnS) and fluorite (CaF_2) (Direction des Mines et de la Géologie, DMG, 1982). After the closure of most of the mines, wastes (rock dumps, flotation tailings, smelting scoria) are forsaking in agricultural areas without any environmental concern. Several studies showed that the mining discharges represent a potential source of contamination for soils (Lee et al., 2001; Sastre et al., 2004; Ferreira Da Silva et al., 2005; Lin et al., 2005; Diţoiu & Oşean, 2007; Galfati et al., 2011).

This contamination, which can persist for a long period (Marcus, 1997), can affect the vegetation (Conesa et al., 2006) and the food chain (Kabata-Pendias & Pendias, 1992; He et al., 2005), is a source of serious ecological problems (Mikanova, 2006). Consequently, it is of great importance to estimate the total contents of toxic elements and their speciation in these soils. The speciation is a technique developed to identify the phases to which metals can possibly be fixed (Kot & Namiesnik, 2000).

So, metals, which are bounded to the most soluble fractions, represent the bioavailable phase which may contribute to the contamination of deep soil, water and floras.

The Jebel Hallouf-Sidi Bouaouane mining area, is composed from two districts (Jebel Hallouf and Sidi Bouaouane), and is situated in the Northwest of Tunisia, at 140 km from Tunis city (Fig. 1). From 1899 to 1986, these districts produced more than 525,000 tons of Pb and 81,000 tons of Zn metal (DMG, 2003). Ore processing produced several million tons of wastes (rock dumps, flotation tailings, smelting scoria), stored inside the mining perimeter, on the watersheds of the local river system and in the middle of farmlands intended for the culture of cereals (barley) and vegetables (Bean, Fennel, Radish, Swiss chard, etc.).

Using mineralogical, geochemical and statistical (PCA) analysis, the objectives of our study are: (i) to characterize the flotation tailings, which are the main source of contamination in the area, (ii) to determine the horizontal distribution of heavy metals in the surrounding soils, and (iii) to assess the bioavailability of metals in these soils by the use of batch leaching tests.

2. DESCRIPTION OF THE STUDY AREA

The study area is characterized (Fig. 2) by a slightly contrasting topography. The slope is dipping to the W to WNW, and the culminating point (348m) is located at Jebel Jebil. The mining district of Jebel Hallouf-Sidi Bouaouane is subdivided in two mining areas; the first one is located on the eastern side of Jebel Hallouf hill, while the second is located in the plain of Sidi Bouaouane. The climate is semi-arid, and is characterized by rainy winters (300 to 600 mm/year and 900 mm/year during flood periods) and warm summer seasons. The annual average temperature and evaporation are 18.4°C and 1585mm/year, respectively. The major wind directions are W-NW and W with an average speed of 19 m/s (calculated for 119 observations).

The Flotation tailings of Jebel Hallouf (two piles "JH-I" and "JH-II") and Sidi Bouaouane (one pile "DBA"), (Figs. 1 and 2), are drained by two watercourses that are active during rainy periods and discharge east of the study area into Wadi Kasseb, a tributary of Wadi Medjerda. This one is the most important river in Tunisia, and the water resources of which are used for both domestic use in several cities and irrigation in the north of Tunisia. The local soils are brown to darkish–brown in colour, making fertile grounds for every type of cultures. Therefore, these soils are used for the culture of cereals (barley and wheat), vegetables (bean) and olive on large plots or for market gardening plants (radish, spinach and fennel) on small ones. The pH of these soils (7.8 to 8.3) is neutral to slightly alkaline.

2.1. Geological setting

The district of Jebel Hallouf-Sidi Bouaouane is located in the southern part of the "Nappes Zone" and in intermediate position between the "Scale Zone" of Aîn El Bey in the south and the Kasseb Unit in the North (Mansouri, 1987). The "Scale Zone" is made of the superposition of Paleocene marls, Eocene limestones and Miocene glauconitic sands and claystones. The Kasseb Unit is mainly composed of Paleocene clays, Ypresian Globigerina limestones and Lutetian clays with yellow carbonate balls (Talbi et al., 2008) (Fig. 2).

Sainfeld (1956) mentioned that this region was affected by a complex tectonic activity, which has induced its subdivision into several compartments delineated by fan-shaped strike-slip faults, trending NE-SW at first and E-W later on (Fig. 2).

2.2. Mineralization

The district includes two types of mineralizations (Sainfeld, 1952; Mansouri, 1980);

i) Those associated with the post-nappes Neogene strata, the Neogene conglomerates and the Eocene substratum at Sidi Bouaouane, where two mineralized areas are distinguished: Sidi Bouaouane s.s (Site 8) in the south and Kadhkadha (Site 7) and "Peperino" (site 6) to the north.

ii) Those occurring as vein and karst fillings at Jebel Hallouf. These mineralised bodies are in discordance with the Senonian limestones, which make the local substratum of the Miocene (Rouvier, 1971). Mineralization, wich occur within intra-Senonian veins (transverse faults) and karsts, is associated to the Campanian-Maastrichtian massive limestone bar, extending almost over three kilometres. The ore was mined through five sites (Fig. 2), wich are from West to Est: the Calamine quarter (site 1), the Western quartier (site 2), the Furkas quartier (Main shatfs; Site 3), the Attilio quartier (site 4) and the Palmier quartier (site 5).

3. MATERIAL AND METHODS

3.1. Sampling

Flotation tailings were taken each 2 metres from base to top along the side of the tailings pile.

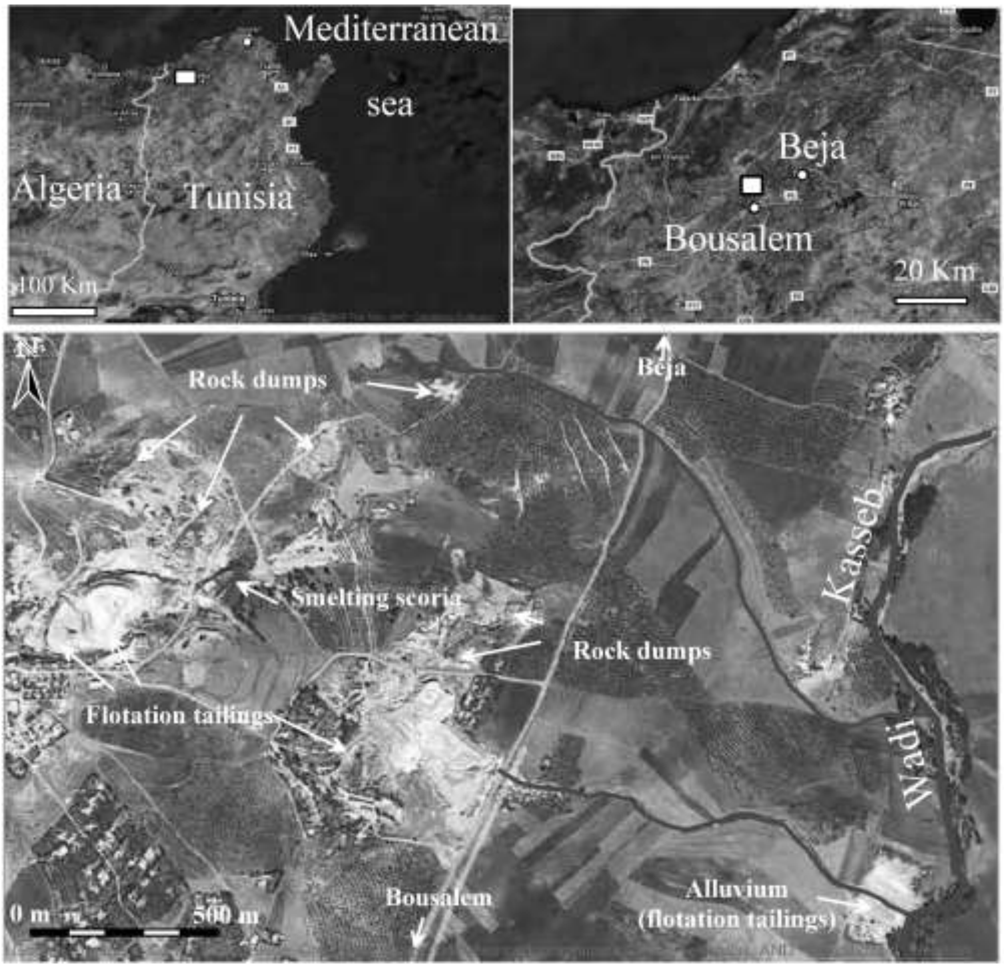

Figure 1. Satellite view of the Jebel Hallouf-Sidi Bouaouane mining area and location of the different contamination sources.

Topsoil (0-20 cm in depth) samples were collected systematically in both of the mining areas around the tailing piles, according to a sampling network established on a 250m-250m grid (Fig. 3). All sampling points were geo-referenced by Global Positioning System (GPS). The total of 99 topsoil samples was collected over an area of 8.75 km^2 (3.5 km x 2.5 km). Five-control soil samples were also collected from non-contaminated areas located North-Est and South-West of the mining district. All samples were stored in polyethylene bags.

To study the mobility of heavy metals using batch testing, samples were analysed as follows: three tailings samples from the two flotation tailings dumps I and II of Jebel Hallouf (BAI-3 and BAII-4, respectively), and that of Sidi Bouaouane (DBA-5). Four contaminated soil samples (S21, S31, S56 and S85), were collected. The first in the vicinity of the flotation tailing dump (S21), the second near the rock dumps (S31), the third in the watercourse that drains the tailings pile of Sidi Bouaouane (S85) and the fourth at the confluence between the latter watercourse and the Wadi Kasseb (S56). One control sample (S71) was collected far from the mining area, at 7 km to the North (Figs. 1 and 3).

The bio-available heavy metals such as Zn, Cd, Pb and Cu were extracted with a $Ca(NO_3)_2$ solution (0.001 M). For each sample, a mixture of 50 g of tailing/soil and $Ca(NO_3)_2$ solution (1:1) (w:w) was prepared. Samples were subjected to a continuous stirring during 48 hours with a rotation of 15 rpm for nine successive cycles. Samples were then spin-dried during 20 min (3000 rpm) and filtered (Whatmann N° 542) for the analysis of Pb, Zn, Cd and Cu. A series of geostandards (BEN, DRN and GSN) were analyzed to assess the accuracy of the results provided by the analytical equipments.

All the geochemical data were used to establish Pb, Zn, Cd and Cu distribution maps across the mining sites.

The mineralogical study were conducted by Scanning Electron Microscopy (SEM Type JEOL, JSM-840 Scanning Microscopy in the Centre SPIN of the National School of Mines in Saint-Etienne) on polished sections of rock dumps and tailings samples. Results were given as micrographs and element distribution maps.

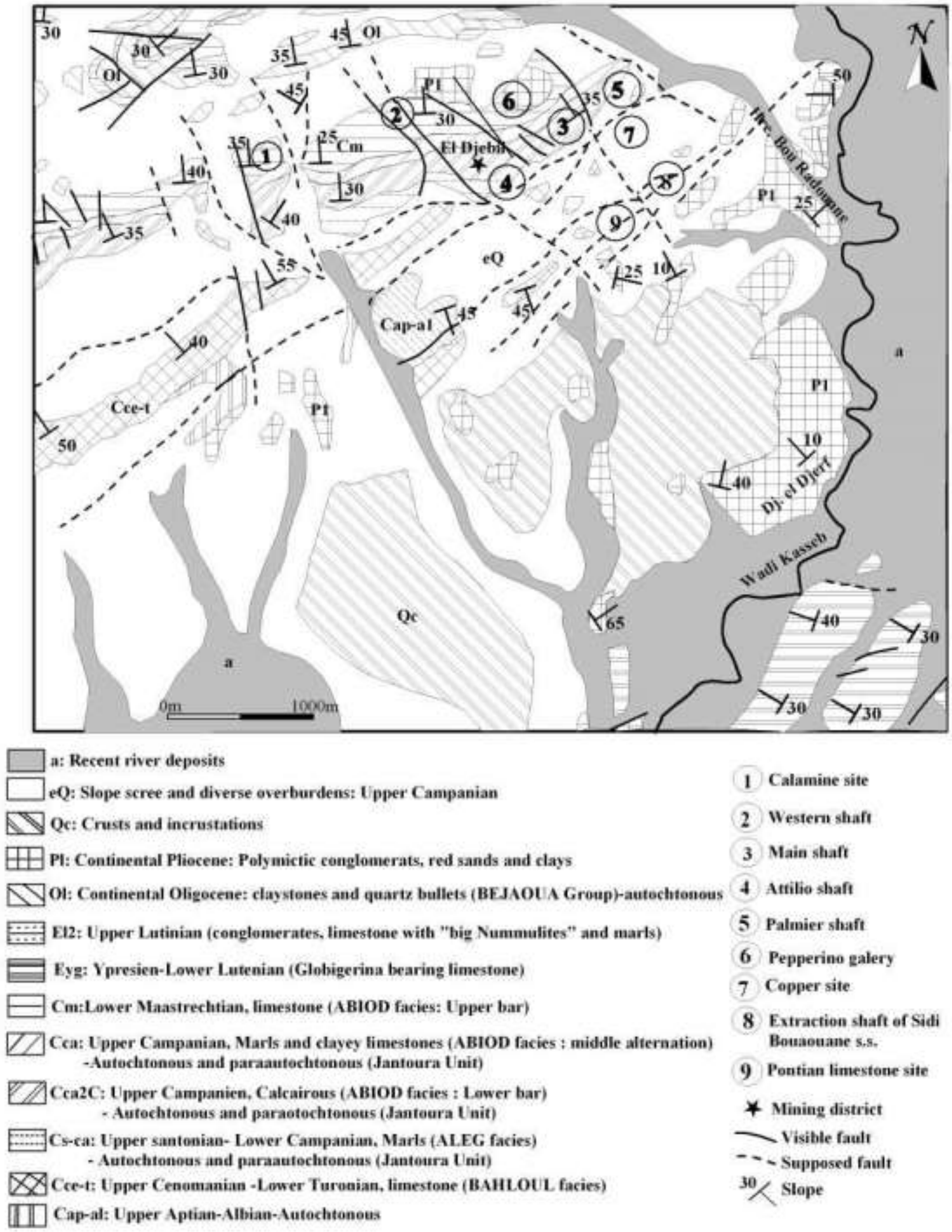

Figure 2. Geologic map of the study area (OTC, 1995) and location of ore and extraction sites (after Sainfeld, 1952).

3.2. Preparation and analyses

Samples were dried in the oven at 50°C during 48 hours and then sieved to 2 mm mesh. The fraction < 2 mm was used for chemical analysis after grinding in an agate mortar. For the analysis of heavy metals (Pb, Zn, Cd and Cu), 150 mg of the samples were digested by triacid (HCl-HNO_3-HF) for analysis by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy, HORIBA-JOBIN YVON, type Activa) in the Laboratory GENERIC of the National School of Mines in Saint-Etienne. For each sample, and to quantify the major elements (Fe, Al, Ca, Mg, Na, K, P) a pearl was prepared (400 mg of Lithium Nitrate and 7.2 g of di-lithium tetraborate are added to the 400 mg. of powdered sample) by fusion and analyzed by wavelength dispersion X-ray fluorescent spectrometry (XRF, BRUKER, type SRS 3400, in the Laboratory GENERIC of the National School of Mines in Saint-Etienne).

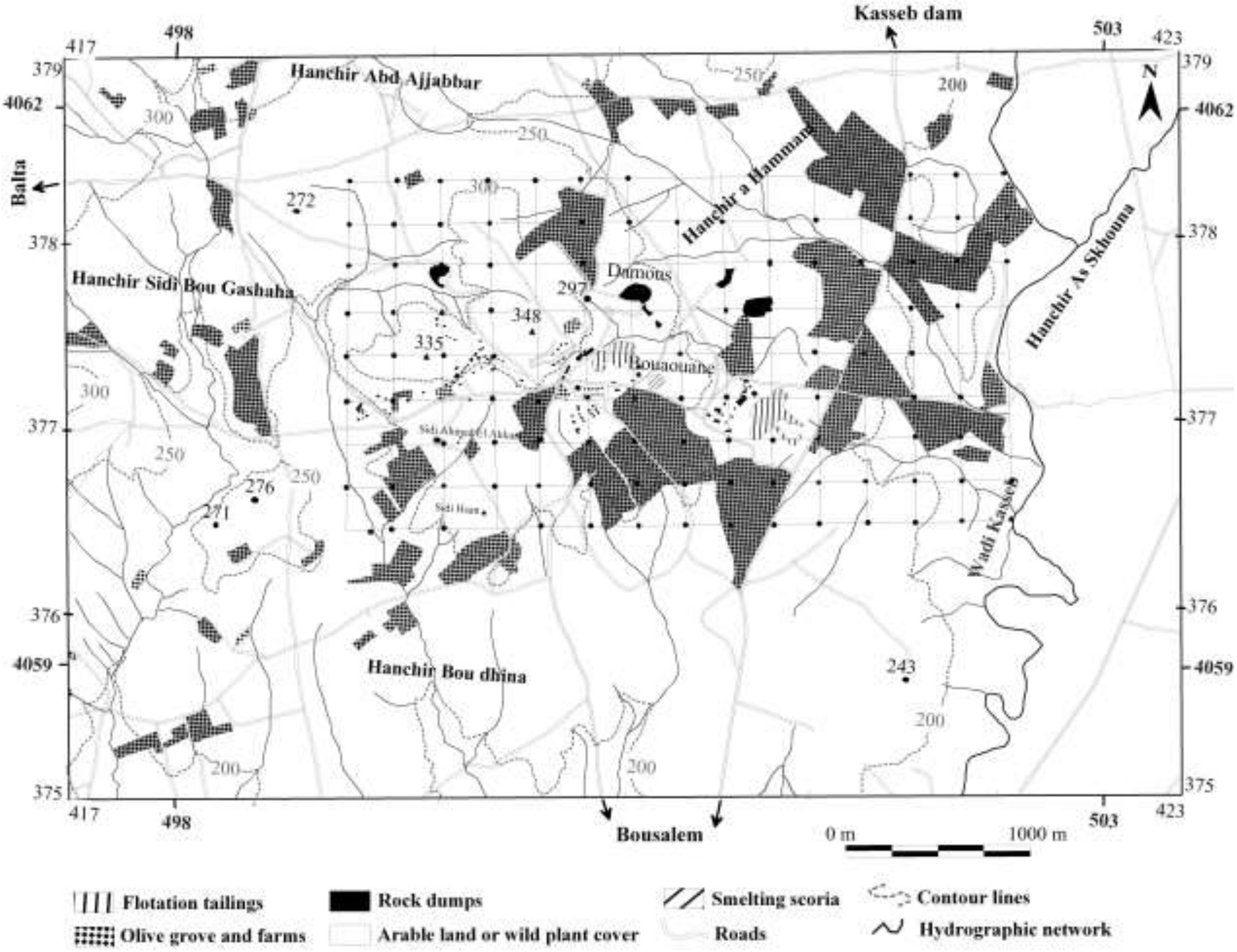

Figure 3. Topographic and study grid maps of Bouaouane area (After the topographic map of Bousalem to 1/25000; OTC, 1989).

3.3. Enrichment Index (EI), Enrichment Factor (EF), statistical analysis and Principal Component Analysis (PCA)

The Enrichment Index (EI) was calculated to estimate the degree of soil contamination (Nishida et al., 982; Chon et al., 1995; Kim et al., 1998; Lee et al., 1998) and to establish the spatial distribution of heavy metals in the study area. This index was calculated according to the formula of Ferreira Da Silva et al., (2005) modified for four elements (Pb, Zn, Cd and Cu):

$$\mathbf{EI = (([Pb] / 100) + ([Zn] / 300) + ([Cd] / 2) + ([Cu] / 100))/4}$$

A common approach to estimate the anthropogenic impact on soils is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Salomons & Förstner 1984; Dickinson et al., 1996; Hornung et al. 1989). The EF method normalizes the measured heavy metal content in the soil sample with respect to a reference metal such as Fe or Al (Ravichandran et al., 1995). In this respect, the EF was considered according to the following equation:

$$\mathbf{EF = ([ME] / [Al])_{mining\ area} / ([ME] / [Al])_{control},}$$

where [ME] is the concentration of metal element and [Al] the concentration of aluminium oxid-hydroxide in soil.

Statistical analysis were applied for the interpretation of analytical results of heavy metals and major elements in flotation tailings and soil and PCA was used to constrain the origin of the contaminants in soil (software: STAT*lab*™, version 2.0., Générique STATlab).

4. RESULTS

4.1. Analysis of flotation tailings

4.1.1. Granulometry and mineralogy

The flotation tailings of the dump of Bouaouane (DBA) are dominated (up to 90 %) by fine particles (< 63 μm); those of Jebel Hallouf

(DJH-I) are dominated by sand sized fraction (up to 80%).

The tailings are very rich in sulphides (galena, jordanite, sphalerite, pyrite, marcasite), oxi-hydroxides (goethite, hematite), carbonates (cerussite, smithsonite) and sulphates (anglesite, barite). Minor metallic phases are also present in the tailings such as iron carbonates (e.g. siderite), copper sulfides (e.g. chalcopyrite) and copper sulfosalts (e.g. tennantite) (Fig. 4). The gangue is dominated by calcite, with small amounts of clay minerals (kaolinite and illite).

4.1.2. Chemical analysis

The results of chemical analysis show (Table 1) that the flotation tailings are highly concentrated in Pb, Zn, Cd and Cu at Jebel Hallouf (9,200 $mg\cdot kg^{-1}$, 8,200 $mg\cdot kg^{-1}$, 66.5 $mg\cdot kg^{-1}$ and 115.5 $mg\cdot kg^{-1}$, respectively) and Sidi Bouaouane as well (16,900 $mg\cdot kg^{-1}$, 26,750 $mg\cdot kg^{-1}$, 211.5 $mg\cdot kg^{-1}$ and 95 $mg\cdot kg^{-1}$, respectively). These results show that the flotation tailings of Sidi Bouaouane, which contain higher amounts of clayey fraction, are more concentrated in heavy metals than those of Jebel Hallouf (Table 1).

Table 1. Concentration ($mg\cdot kg^{-1}$) of heavy metals in the flotation tailings of Jebel Hallouf-Sidi Bouaouane.

	Jebel Hallouf			Sidi Bouaouane		
	Min	Max	Mean	Min	Max	Mean
Pb	1,800	16,700	7,663 ±4,934	2,300	36,900	10,018 ±10,731
Zn	2,900	13,500	7,577 ±2,469	6,900	46,600	14,287 ±12,410
Cd	23	110	62.6 ±16.4	28	395	100 ±112
Cu	49	182	77.7 ±32.5	28	162	61.6 ±39
Mean:17 samples for Jebel Hallouf and 7 samples for Sidi Bouaouane						

4.1.3. Statistical analysis and PCA

The statistical analysis shows (Table 2) a good correlation, between heavy metals (Cd, Zn, Pb), Al_2O_3 and CaO. Positive correlations are highlighted between heavy metals (r_{Cd-Pb}=0.963, r_{Cd-Zn}= 0.818, r_{Zn-Pb}=0.784) on one hand and between these elements and Al_2O_3 ($r_{Zn-Al2O3}$=0.804, $r_{Cd-Al2O3}$= 0.740, $r_{Pb-Al2O3}$=0.712) on the other hand. These results give evidence of the high affinity between heavy metals, and between these elements and the clayey fraction.

Negative correlations are significant between heavy metals and CaO (r_{Zn-CaO}= 0.652, r_{Cd-CaO}= 0.692, r_{Pb-CaO}= 0.705), showing a lack of affinity between heavy metals and carbonate fraction. The bimodal geochemical character of the tailings material is ascribable to their high contents in both clay and carbonate fractions.

The PCA representation, in which the major first three components or factors (F1, F2 and F3), represent alone more than 83.5 % of the variance, shows:

i) According to the factor F1 (55.9 %), an association between the heavy metals (Cd, Pb, Zn) and Al_2O_3, which reflects the mineralogy of clays.

ii) According to the factor F2 (17.8 %), a similar behaviour of Fe_2O_3 and Cu is highlighted, which suggests that copper is associated to iron oxi-hydroxides.

iii) According to the factor F3 (9.8 %), the Mn and Fe oxides behave similarly in the tailings pile.

4.2. Soil analysis

4.2.1. *Heavy metal contents and distribution*

Lead (Pb) concentrations (Table 3) range between 31 $mg\cdot kg^{-1}$ and 39,720 $mg\cdot kg^{-1}$ with an average value of 651.56 $mg\cdot kg^{-1}$. However, it is worthy to note that contamination by this element is more important in soils neighbouring the tailings piles and the smelting (scoria) wastes at Jebel Hallouf where Pb-mineralization (galena) predominates.

Strong concentrations have been recorded for Zn (up to 9,000 $mg\cdot kg^{-1}$), with an average value of 517.32 $mg\cdot kg^{-1}$. Samples that are most contaminated by this element were taken (Fig. 3) in the neighbourhood of the Zn-hydroxide workings (site 1), the western well (site 2), the Attilio well (site 4), and in the northern (site 8) and the eastern areas of Sidi Bouaouane district near Wadi Kasseb.

Very high concentrations are recorded for Cd (7.1 $mg\cdot kg^{-1}$ to 86.2 $mg\cdot kg^{-1}$). The samples located below the wind and runoff (samples S21, S31 and S56) have a larger amounts of Cd, are more concentrated than others taken in soils located north of the study area (sample S71).

The concentrations of Cu throughout the whole area range from 13 $mg\cdot kg^{-1}$ to 131 $mg\cdot kg^{-1}$. The highest values (more than 50 $mg\cdot kg^{-1}$) are recorded for those areas bearing high concentrations in Pb, Zn and Cd.

The Pb and Zn maps (Fig. 5) show three areas highly concentrated in these metals, the first one is located West of the study area, the second in its middle near the sources of contamination and the last one to the East, near Wadi Kasseb. The dispersion axis is elongated in the West-East direction. Another small area is characterized by high contents in Pb, Zn and Cd is identified in the South-West of the study area.

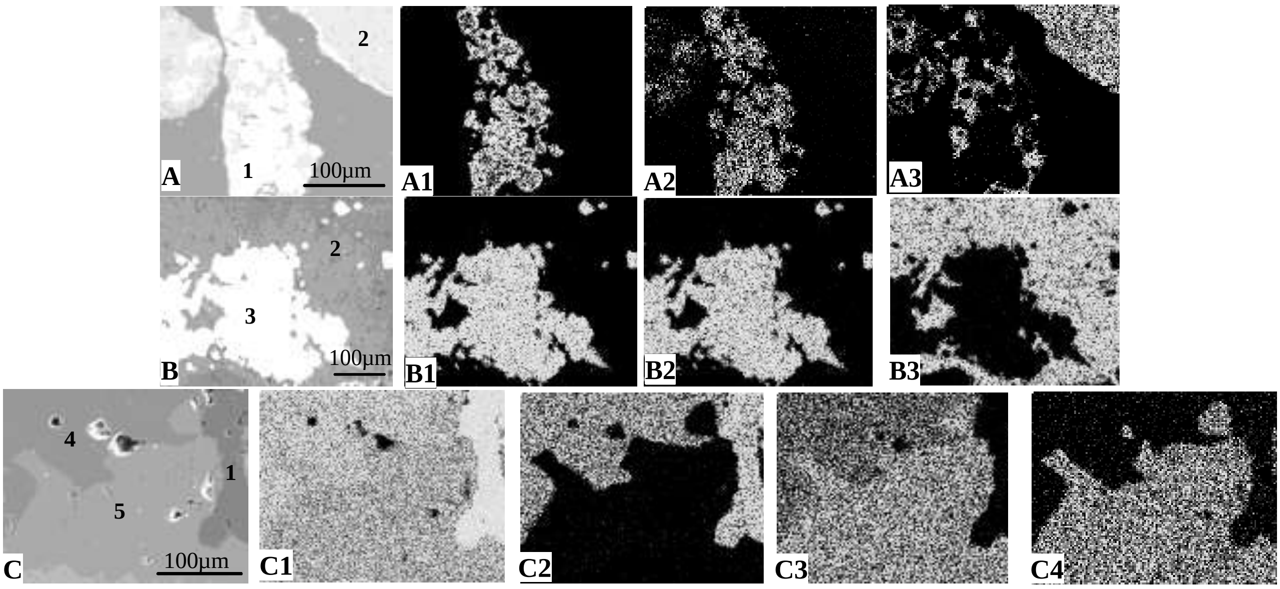

Figure 4. SEM analysis of flotation tailings from Jebel Hallouf mining area (A: sample BAII-3, tailings heap I; B and C: samples S4 and S2, extraction waste). A: Backscattered electron image (330x magnification); A1, A2 and A3: distribution maps of sulphur, lead and calcium respectively. B: Backscattered electron image 100x magnification); B1, B2 and B3: distribution maps of lead, sulphur and calcite respectively; C: Backscattered electron image (170x magnification); C1, C2, C3: distribution maps of sulphur, iron, copper and arsenic respectively. 1: Pyrite (FeS_2), 2: Calcite ($CaCO_3$), 3: Galena (PbS), 4: Chalcopyrite ($CuFeS_2$), 5: Tennantite ($Cu_{12}As_4S_{13}$).

Table 2. Correlation between heavy metals (Cd, Cu, Zn and Pb) and majors elements (Al_2O_3, Fe_2O_3, MnO and CaO) in the flotation tailings of Jebel Hallouf-Sidi Bouaouane mining area (n : number of samples).

N=28	Cd	Cu	Zn	Pb	Al_2O_3	Fe_2O_3	MnO	CaO	F1	F2	F3
Cd	1								**0.932**	0.096	0.073
Cu	0.101	1							0.056	**0.886**	-0.048
Zn	**0.818**	-	1						**0.887**	0.104	0.095
Pb	**0.963**	-	**0.784**	1					**0.904**	-0.075	0.208
Al_2O_3	**0.740**	-	**0.804**	**0.712**	1				**0.905**	-0.002	0.069
Fe_2O_3	-0.278	**0.372**	-0.174	-0.334	***-0.380***	1			***-0.429***	**0.685**	**0.416**
MnO	***-0.514***	-0.238	***-0.502***	***-0.344***	***-0.431***	0.218	1		***-0.557***	-0.319	**0.724**
CaO	***-0.692***	-0.109	***-0.652***	***-0.705***	***-0.843***	**0.406**	0.255	1	***-0.842***	0.054	-0.215
Variance %									55.9	17.8	9.8

Table 3. Variation of Pb, Zn, Cd and Cu concentrations ($mg \cdot kg^{-1}$) in soil samples.

	Min-Max n= 99	LGB (1)	Canadienne recommendations (2)	Target values (3)
Pb	31- 39,720 (651.56±1.08)*	42 ± 12	70	85
Zn	112.3- 9,030 (517.32±1.00)*	126 ± 15	200	140
Cd	4.8-68 (10.17±1.08)*	0.62 ± 0.35	1.4	0.8
Cu	13.6- 130.7 (27.50±1.09)*	52 ± 13	63	36

(1) Local Geochemical Backround calculated from six representative soil samples.
(2) Agricultural soils, 1999.
(3) Target values for french soil/sediments, ADEM 2005.
* : Geometric Mean ± Geometric Deviation

The Cd map (Fig. 5) shows that high concentrations in this element are more widespread than for Pb and Zn, covering almost the totality of the study area. The Cu map shows that concentrations making no more than three times the LGB (up to 130 $mg \cdot kg^{-1}$) are circumscribed in areas located north of the study area and near the rock dumps (Fig. 5).

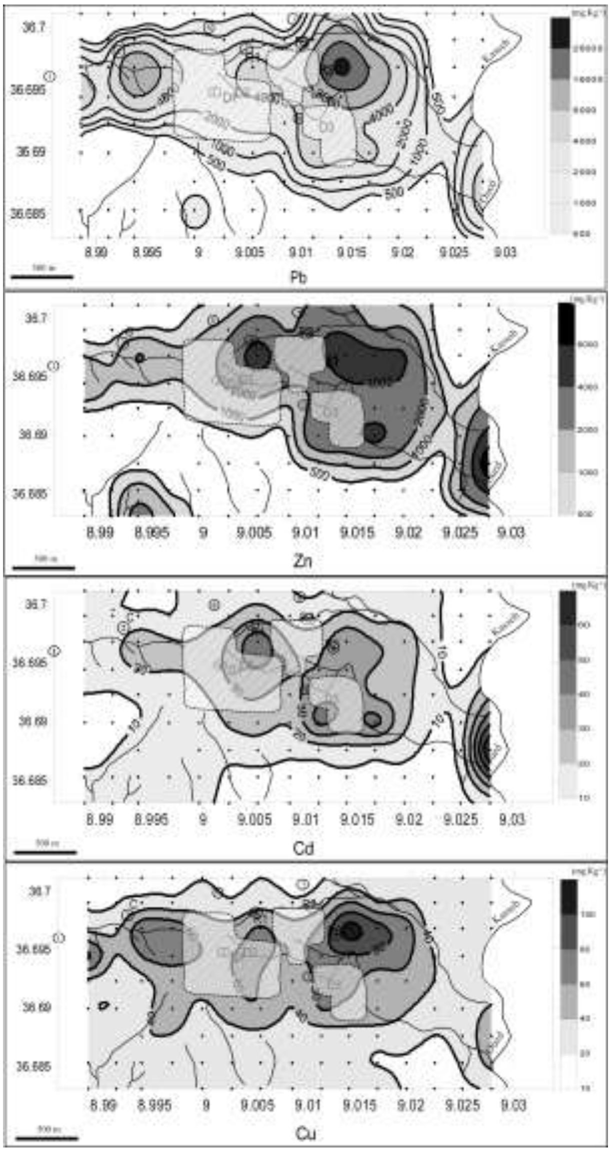

Figure 5. Distribution maps of Pb, Zn, Cd and Cu concentrations in the topsoil of Jebel Hallouf-Sidi Bouaouane area. Hatched areas are zones extrapolated by the software.

4.2.2. Enrichment Factor (EF)

All the samples (S21, S31, S56 and S85) taken near the flotation tailing dumps (Table 4), which are contaminated by Cd, Pb and Zn, have high EF values (Table 5). These values (60 to 817 for Cd, 192 to 916 for Pb and 42 to 436 for Zn) are very high in respect to those of the uncontaminated sample (S71) (12, 5 and 1.5, respectively).

For Cu, all EF values (Table 5) range between 1 and 6 for the contaminated samples (S21, S31, S56, Table 4) and lower than 1 for the uncontaminated one.

4.2.3. Statistical analysis and PCA

The statistical analysis of major elements and heavy metal contents (Table 2 and 6) in soil samples shows positive correlations: (i) for Cu with respect to MnO on one hand, and (ii) for heavy metals (Pb, Zn and Cd) between each other on the other hand (Table 6). These correlations suggest a high affinity of Cu to Mn-oxides while for heavy metals it gives an evidence of their common source and/or the similarity of their geochemical behaviour.

Taking into consideration the major first three factors (F1, F2 and F3), which represent more than 86.7 % of the variance altogether, the PCA (Table 6) shows that:

i) According to the first factor (F1= 50.6 %), it can be noticed an association between heavy metals and oxides (MnO, Fe_2O_3), on one hand, and a separation between CaO and the other elements, on the other hand.

ii) According to the second factor (F2=28.6%), a relationship between Cd, Zn and CaO and another one between Al_2O_3 and Fe_2O_3 can be observed.

iii) According to the third factor (F3 = 7.5 %), a separation between Pb and the other elements is noticed. This observation shows that lead behaves differently with respect to the other elements.

In addition, the F1xF2 and F1xF3 diagrams show (Figs. 7 and 8) that: (i) F1 separates between two poles corresponding to two types of soils, the first being rich in carbonates (high CaO contents) and the second being rich in clays (high Al_2O_3 contents), (ii) F2 separates between the contaminated soils (rich in heavy metals) and those uncontaminated, and (iii) F3 separates between the soils mainly contaminated by Pb, Zn and Cd. Those contaminated by Pb are located near the smelting (scoria) wastes and the extraction shafts and those mainly contaminated by Zn and Cd are located near the flotation tailings dumps.

Table 5. Enrichment Factor (EF) for some soil samples from the study area (sample location is the same as in Table 4).

Sample	Metal			
	Cd	Cu	Pb	Zn
S21	104	2	271	46
S31	60	2	814	42
S56	817	6	916	436
S85	82	1	192	49
S71	12	0.4	5	1.5

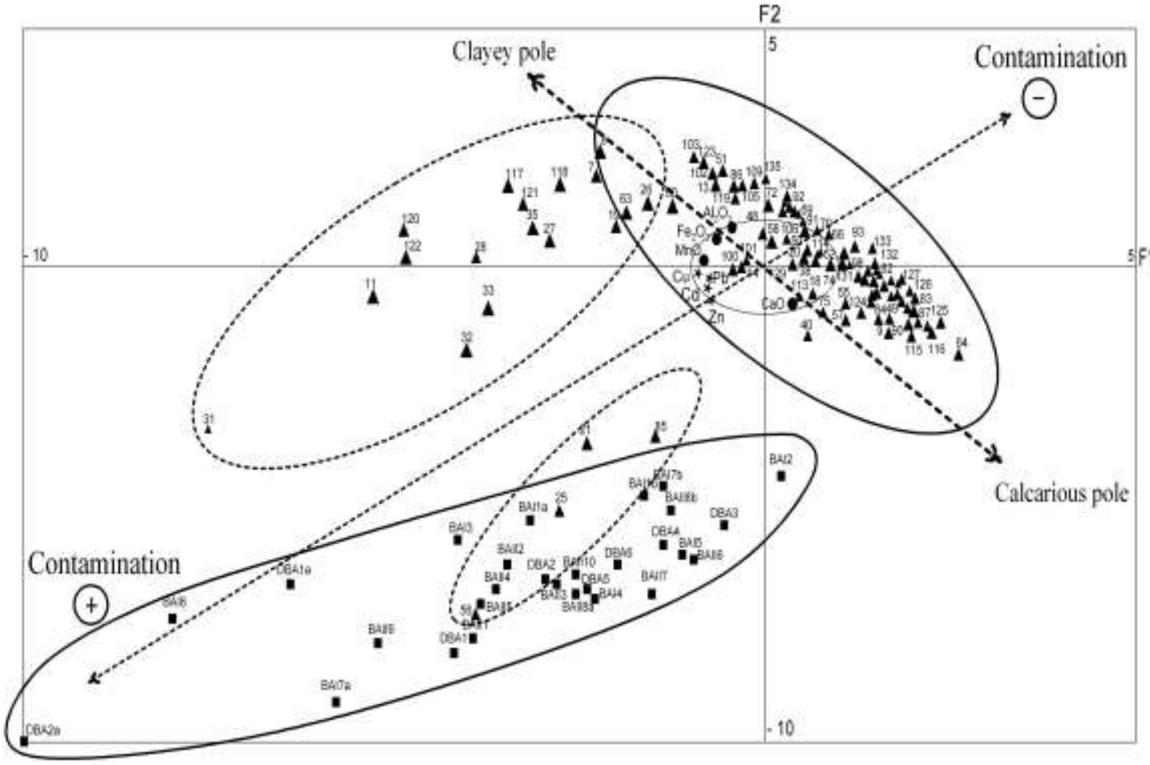

Figure 7. PCA diagram of soil samples (triangles) according to the F1xF2 axes. The variables are the heavy metal (stars) and major elements (circles). Tailing samples (squares) are the anonymous individuals.

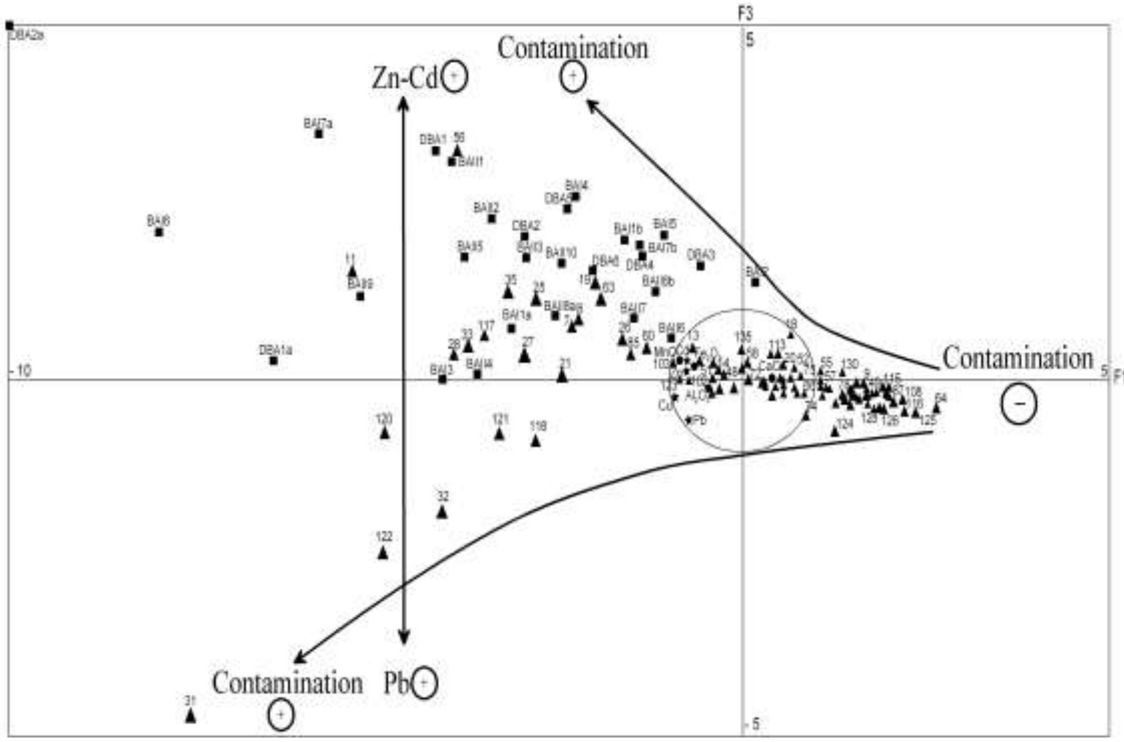

Figure 8. PCA diagram of soil samples (triangles) according to the F1xF3 axes. The variables are the heavy metal (stars) and major elements (circles). Tailing samples (squares) are the anonymous individuals.

4.3. Heavy metals leaching test (Batch)

4.3.1. *Flotation tailings*

The experiments were conducted on three samples representative of the two tailing piles of Jebel Hallouf (BAI-3 and BAII-4), and that of Sidi Bouaouane (DBA-5). The concentrations of Pb, Zn, Cd and Cu in the batch solutions (Table 7) show that the concentrations of zinc and cadmium are more elevated for the samples BAII-4 (3,060$\mu g \cdot l^{-1}$ and

2.5$\mu g \cdot l^{-1}$, respectively) and DBA-5 (2,261$\mu g \cdot l^{-1}$ and 1.9$\mu g \cdot l^{-1}$, respectively) than for the sample BAI-3 (543$\mu g \cdot l^{-1}$ and 0.2$\mu g \cdot l^{-1}$, respectively). However, the concentrations of Pb (36.6$\mu g \cdot l^{-1}$ to 51.2$\mu g \cdot l^{-1}$) and Cu (14.4$\mu g \cdot l^{-1}$ to 18.5$\mu g \cdot l^{-1}$) are confined to narrow ranges in all samples.

Table 7. Mean concentration ($\mu g \cdot l^{-1}$) of Cd, Cu, Pb and Zn in the solutions of batch testing conducted on typical flotation tailings samples.

Tailing sample		Metal			
Ref.	Dump	Cd	Cu	Pb	Zn
BAI-3	I- Jebel Hallouf	0.2	14.4	46.4	543
BAII-4	II- Jebel Hallouf	1.9	18.5	36.6	2,261
DBA-5	Sidi Bouaouane	2.5	17.2	51.2	3,060

4.3.2. Soils

The experiments were conducted on the four contaminated soil samples considered in this study (Table 4). These sample are collected in the vicinity of the flotation tailing piles (S21) and rock dumps (S31), in the watercourse which drains the tailings pile of Sidi Bouaouane (S85) and at the confluence between the latter watercourse and Wadi Kasseb (S56) (Figs. 1 and 3). To compare these samples, one control sample (S71) has been analysed.

The concentrations of Pb (400 $\mu g \cdot l^{-1}$, 483$\mu g \cdot l^{-1}$, 342 $\mu g \cdot l^{-1}$ and 16.9$\mu g \cdot l^{-1}$, respectively), Zn (906$\mu g \cdot l^{-1}$, 63 $\mu g \cdot l^{-1}$, 650 $\mu g \cdot l^{-1}$ and 3,240 $\mu g \cdot l^{-1}$, respectively), and Cd (5.8 $\mu g \cdot l^{-1}$, 2 $\mu g \cdot l^{-1}$, 9.8 $\mu g \cdot l^{-1}$ and 3.2 $\mu g \cdot l^{-1}$, respectively) in the batch solutions (Tab. 8) of these soils are very high with respect to those in the control sample (S71), where Pb, Zn and Cd are equivalent to 25.2 $\mu g \cdot l^{-1}$, 40.2 $\mu g \cdot l^{-1}$ and 0.9$\mu g \cdot l^{-1}$, respectively.

5. DISCUSSION

5.1. Mining wastes

The flotation tailings under concern bear high concentrations in Pb (1,800 to 36,900 $mg \cdot kg^{-1}$), Zn (2,900 to 46,600 $mg \cdot kg^{-1}$) and Cd (23 to 395$mg \cdot kg^{-1}$). These elements are associated to sulphides, mainly galena and sphalerite. These minerals present in the flotation tailings, have been identified by SEM and metallographic observations. The study of other mining districts located in the northwest of Tunisia (Babbou-Abdelmalek et al., 2011; Boussen et al., 2010; Ghorbel et al., 2008 and 2010; Mlayah et al., 2009; Othmani et al., 2007; Souissi et al., 2008) confirm that the flotation tailings there are also rich in heavy metals, essentially Pb, Zn and Cd. The PCA analysis (Table 2) shows according to the first factor (F1) that at a rate of 56% variance, an affinity between heavy metals (Cd, Zn, Pb) and Al_2O_3, which confirms the good positive correlation so described.

Table 4. Concentrations of heavy metals and major elements in soil samples of the study area (sample location is illustrated in figurea 1).

Sample	Sample location	Concentration ($mg \cdot kg^{-1}$)				Concentration (% oxyde)			
		Pb	Zn	Cd	Cu	Al_2O_3	Fe_2O_3	MnO	CaO
S21	Near Sidi Bouaouane tailing	8,566	4,435	53.0	72.7	8.3	5.9	0.09	25.0
S31	Near rock dumps	39.7	6,276	44.6	130.7	12.0	8.3	0.18	10.4
S56	Near Wadi Kasseb	5,963	9,030	86.2	55.6	1.7	6.6	0.21	43.4
S85		6,087	4,704	38.4	53.5	8.4	4.7	0.11	26.2
S71	Uncontaminated area	36	152	7.1	20.0	8.8	5.2	0.05	16.1

Table 6. Correlation between heavy metals (Cd, Cu, Zn and Pb) and the major elements (Al_2O_3, Fe_2O_3, MnO and CaO) in soil samples and PCA analysis results (n: number of samples).

N= 99	Cd	Cu	Zn	Pb	Al_2O_3	Fe_2O_3	MnO	CaO	F1	F2	F3
Cd	1								**0.775**	***-0.494***	0.260
Cu	**0.686**	1							**0.925**	-0.107	-0.204
Zn	**0.886**	**0.659**	1						**0.737**	***-0.571***	0.146
Pb	**0.588**	**0.796**	**0.636**	1					**0.734**	-0.323	***-0.573***
Al_2O_3	**-0.029**	**0.343**	-0.109	0.127	1				**0.461**	**0.800**	-0.102
Fe_2O_3	**0.355**	**0.519**	0.185	0.233	**0.694**	1			**0.679**	**0.539**	0.228
MnO	**0.565**	**0.743**	**0.555**	**0.414**	**0.393**	**0.541**	1		**0.831**	0.091	0.270
CaO	0.097	-0.265	0.093	0.080	***-0.757***	***-0.613***	***-0.397***	1	***-0.409***	***-0.803***	0.076
Variance %									50.6	28.6	7.5

The second factor (F2) with an 18 % rate of variance highlights the affinity of copper to iron oxide (Fe_2O_3). Such a statement can be justified by the capacity of iron oxide to absorb copper, present in the tailings. The third factor (F3) with a 10 % rate of variance shows that an affinity exists between iron and manganese oxi-hydroxides

The positive correlation found between the heavy metals and Al_2O_3 suggests that clays have high fixation capacity for metals. In fact, Alloway (1995) advances the idea that clay minerals can develop large specific area, as high as 700-800 $m^2 \cdot g^{-1}$ and possess important properties of absorption and adsorption. On the other hand, the high carbonate content, even higher than the clay content, is essentially related to the carbonated nature of the ore host-rocks. The correlation observed between heavy metals and CaO suggests a relation between these two components in spite of the negative trend. The presence of carbonates makes the pH alkaline, which facilitates all the modes of fixation of the toxic elements, and the surface of carbonate minerals may also play a role in sorption processes.

The concentrations of Pb, Zn and Cu measured in the batch solutions of the flotation tailings samples (36.6 $\mu g \cdot l^{-1}$ to 51.2 $\mu g \cdot l^{-1}$, 543 $\mu g \cdot l^{-1}$ to 3060 $\mu g \cdot l^{-1}$ and 14.4 $\mu g \cdot l^{-1}$ to 18.5 $\mu g \cdot l^{-1}$, respectively; Table 8) are higher than those measured in the meteoric water samples recovered at the top of the considered three tailings piles, for which Zn concentrations range between 145 $\mu g \cdot l^{-1}$ and 1,933 $\mu g \cdot l^{-1}$ while those of Pb and Cd are below the detection limits of the analytical method. It is worthy to note, however, that Cd concentrations in the batch solutions (0.2 $\mu g \cdot l^{-1}$ to 2.5 $\mu g \cdot l^{-1}$) are lower than those measured in the afore mentioned meteoric water samples (4.6 $\mu g \cdot l^{-1}$ to 34.6 $\mu g \cdot l^{-1}$; Table 8).

Table 8. Mean concentration ($\mu g \cdot l^{-1}$) of heavy metals in batch solution of typical soil samples (sample location is the same as in Table 4).

Sample	Metal			
	Cd	Cu	Pb	Zn
S21	5.8	44.1	400	906
S31	2.1	27.6	483	62.9
S56	3.2	16.2	16.9	3245
S85	9.8	40.9	342	650
S71	0.9	35.5	25.2	40.2

Using the same technique, Souissi et al., (2013) gave similar results for Pb, Zn and Cd concerning batch tests conducted on flotation tailings of other localities in North Tunisia, such as Jebel Ressas (up to 2,402 $\mu g \cdot l^{-1}$, 15.5 $\mu g \cdot l^{-1}$ and 22.6 $\mu g \cdot l^{-1}$, respectively), Sakiet Sidi Youssef (up to 2,629 $\mu g \cdot l^{-1}$, 19.1 $\mu g \cdot l^{-1}$ and 40.5 $\mu g \cdot l^{-1}$, respectively) and Jebel Touiref (up to1,309 $\mu g \cdot l^{-1}$, 10.7 $\mu g \cdot l^{-1}$ and 10.7 $\mu g \cdot l^{-1}$, and, respectively). For the latter locality, slightly higher concentrations are reported for the same elements (up to 3,300 $\mu g \cdot l^{-1}$ for Zn, 83 $\mu g \cdot l^{-1}$ for Pb and 18 $\mu g \cdot l^{-1}$ for Cd) by Othmani et al., (2013) using weathering cells leaching tests. All these values, and especially those of Pb and Cd, exceeded the background concentrations in the Mejerda River (up to 13.3 $\mu g \cdot l^{-1}$ and 3.04 $\mu g \cdot l^{-1}$, respectively) in northern Tunisia (Sahnoun et al. 2009). It exceeds, also, the permissible maximum limits (10 $\mu g \cdot l^{-1}$ and 5 $\mu g \cdot l^{-1}$, respectively) established for environmental norms (US NPDWS 2003, in Lizarraga-Mendiola et al. 2009) as well as the water quality standard for irrigation for Cd (5 $\mu g \cdot l^{-1}$) in Canada (EAD-Alberta 1999). Consequently, the high concentrations of these elements measured in the batch solution are due to their presence as mobile forms in the mine wastes.

5.2. Soils

For Pb, Zn and Cd, the EF values (Table 3) are very high, excepted for soil sample located under the lee of the dispersion contamination direction, by comparison with the corresponding local geochemical background, the Canadian recommendations (1999) for soils, and the values admitted for the French soils (ADEME, 2005). This is confirmed by Babbou-Abdelmalek et al., (2011) at the district of Fedj Lahdoum in the North-West of Tunisia, were the geochemical analysis of soil has revealed high total contents of Pb, Zn and Cd (3646 $mg \cdot kg^{-1}$, 3,236 $mg \cdot kg^{-1}$ and 17 $mg \cdot kg^{-1}$ respectively).

However, the mean concentration value of copper in soil (35 $mg \cdot kg^{-1}$, Table 3) is lower than its LGB (52±13 $mg \cdot kg^{-1}$) and the Canadian recommendations (1999; 63 $mg \cdot kg^{-1}$), and it is almost equal to the target values admitted in French soils (ADEME, 2005) (36 $mg \cdot kg^{-1}$).

Distribution maps (Figs. 5 and 6) show the main zones concerned with high metal concentrations in soil, which are around the extraction pits, the flotation tailings dumps, the smelting plant and the flood areas below the mining area. These maps draw the same general trend and show an axis of dispersion elongated according to the topographic slope. The river system drains the mine site of Jebel Hallouf in two directions: Wadi Kasseb to the East, and the secondary hydrographic system which flows westward. The dominance of the eastward dispersion is noticed near the confluence with Wadi Kasseb as illustrated by satellite images (Fig. 1) as well as the geochemical results of soil analyses (Table 3). These observations are confirmed by the EI map, which highlights, also, a North-East axis of metals dispersal, showing that this map is super imposable to those of single metals.

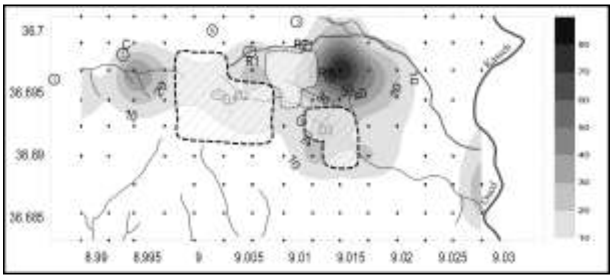

Figure 6. Distribution map of Enrichment Index (EI) of heavy metals in the topsoil of Jebel Hallouf-Sidi Bouaouane area. Points correspond to the location of the collected soil samples. Numbers in circles correspond to the extraction sites according to Sainfeld (1952). Hatched areas are zones extrapolated by the software.

This study shows that all soils located nearby the mine site (rock dumps, flotation tailings, foundry wastes), located both in the flood areas and below the wind are contaminated by metals. The role played by running water, and in a lesser degree by wind, as agents of dispersion and migration of toxic matter (transfer, distribution and mobilization) has been already quoted by other authors (Daniel & Benoît, 2007; Damian et al., 2008); Navarro et al. (2008). These authors devoted their studies to soils developed on carbonated bedrock under similar climatic (semi-arid) conditions near a mining site in Spain. They suggest that rainwater constitute a good means for the dispersal of toxic metals on an immense area and affects, not only groundwater but also the urban and agricultural soils and crops. Several works dealing with contamination of soils by heavy metals near Pb-Zn mineralizations hosted in carbonated rocks in the North of Tunisia (Othmani et al., 2007; Othmani et al.,, 2013; Boussen et al., 2010, Chakroun et al., 2006), in Morocco (Boularbah et al., 2006) and in Spain (Navarro et al., 2008), led to similar results.

The alkaline pH of lands in the neighbourhood of mining sites, due to the high contents of carbonates, plays an important role in the mobility of metals, reducing their transfer in the dissolved state. Such settings are more favourable to mobilisation of metals under particular forms (Navarro et al., 2008).

Despite the important role of carbonates and oxi-hydroxydes to immobilize heavy metals in soil, the batch analysis shows that the soluble forms of heavy metals are not negligible in soil solution. The concentrations of Pb and Cd in the leachates of the contaminated soils (up to 483 $\mu g \cdot l^{-1}$ and 9.8 $\mu g \cdot l^{-1}$, respectively) exceeded the background concentrations in the Mejerda River (up to 13.3 $\mu g \cdot l^{-1}$ and 3.04 $\mu g \cdot l^{-1}$; respectively) in northern Tunisia (Sahnoun et al., 2009). They exceed, also, the water quality standard for irrigation (200 $\mu g \cdot l^{-1}$ and 5 $\mu g \cdot l^{-1}$, respectively) in Canada (EAD-Alberta 1999), or the permissible maximum limits (10 $\mu g \cdot l^{-1}$ and 5 $\mu g \cdot l^{-1}$, respectively) established for environmental norms (US NPDWS 2003, in Lizarraga-Mendiola et al., 2009). For Zn, the concentration in the batch solution (3,245 $\mu g \cdot l^{-1}$) exceeded the background concentrations in the Mejerda River (543 $\mu g \cdot l^{-1}$) in northern Tunisia (Sahnoun et al., 2009), but is comparable to the water quality standard for irrigation (1,000 to 5,000$\mu g \cdot l^{-1}$) in Canada (EAD-Alberta 1999) and the permissible maximum limits (5,000$\mu g \cdot l^{-1}$) established for environmental norms (US NPDWS 2003, in Lizarraga-Mendiola et al. 2009). All these results may be due to the presence of mobile forms in soil solution, essentially for Zn and Cd.

Table 9. Mean concentration ($\mu g \cdot l^{-1}$) of Cd, Cu, Pb and Zn in the batch solutions and meteoric water in mining area.

Water sample	Solid sample	Value	Cd	Cu	Pb	Zn
Batch solutions	Flotation tailings of JH and SBA (n=3)	min.	0.2	14.4	36.6	543
		max.	2.5	18.5	51.2	3,060
		Mean	1.6±0.8	16.7±1.6	44.7±8.7	1,955±1,151
	Soil (n=27)	Min.	0.2	14.6	1.1	8.5
		Max.	9.8	44.1	483	3,245
		Mean	1.7±2.1	22.0±6.9	56±129	236±636
Meteoric water	In contact with the tailing dump II of JH	Top	4.6	<dl	<dl	145
	In contact with the tailing dump of SBA	Top	10.3	<dl	<dl	515
		Bottom	34.6	<dl	<dl	1933
JH: district of Jebel Hallouf ; SBA: district of Sidi Bouaouane ; n: number of tested samples						

Statistical analyses show that correlations are positive ($r > 0.5$) between heavy metals (Zn, Cd Cu) and MnO, which supposes that oxides have a high capacity to fix metals. This statement is confirmed by high values for the F1 parameter in the ACP analysis (Table 6). Several authors (Kabata-Pendias & Pendias, 1992; Sposito, 1989) advance, that in soils of alkaline pH, the oxides of iron, manganese and aluminium, which are present in abundance under amorphous or crystalline forms in the majority of soils, play a dominating role in the sorption of metallic ions. Indeed, Chakroun et al., (2006) have shown that the soil pH at Jebel Hallouf-Sidi Bouaouane mining district is neutral to alkaline (7.8 to 8.3), which confirms the approach of fixation of Cu on iron oxides. This pH interval is the domain of activity of amorphous iron oxides mentioned by Buffle (1988).

The three axial diagrams (F1, F2, F3) of the PCA allowed to show that the heavy metal contaminants originate from both the flotation tailings rich in carbonates and the rock dumps which are very rich in sulphides.

The diagram F1xF2 shows an individualization of two groups of contaminated soils. The first one is representative of soil samples rich in metals and covers the carbonated pole, the latter is occupied by the tailings. Therefore, the tailings material is the first source of contamination by heavy metals. The second group represents soil samples rich in metals but which is in the clay-side pole. In this category, the source of contamination may be attached to the smelting plant and rock dumps (sample S31).

The diagram F1xF3 shows two categories of contaminated soils, the first one represents samples rich in Zn and Cd (S21 and S56) collected near the flotation tailings of Sidi Bouaouane, and the second represents the samples rich in Pb (sample S31) collected near the smelting plan of Jebel Hallouf and the rock dumps, which are very rich in Pb-sulfides.

6. CONCLUSIONS

Mining activities in the district of Jebel Hallouf-Sidi Bouaouane have generated large quantities of wastes (rock dumps, flotation tailings) bearing large quantities of sulphides (galena, sphalerite, pyrite, marcasite) with lesser amounts of chalcopyrite, jordanite, tennantite, barite and siderite, associated to a carbonated (essentially calcite) and clayey (kaolinite and illite) matrix. Alteration during long term superficial exposure has generated supergene minerals such as oxihydroxides (hematite, goethite), carbonates (cerussite, smithsonite) and sulphates (anglesite, gypsum). The statistical analyses show the affinity of heavy metals to clays and carbonates.

Soils in the neighbourhood of the mining area are contaminated by Pb, Zn and Cd, coming from the flotation tailings piles and the rock dumps. The axis of dispersion of metals extends eastward in flood areas along the topographic slope and in the direction of the dominating wind, showing that mine tailings are mobilized as particulate matter by both run off and wind action.

Statistical analysis shows that for soils located near the flotation tailings piles in the study area, contamination by Zn and Cd is more pronounced with respect to Pb, whereas for soils located near the smelting plant of Jebel Hallouf contamination by Pb is more pronounced with respect to Zn and Cd.

The high values of Pb and Cd measured in the solutions of the batch tests operated on flotation tailings and soils, exceed the environmental norms, and, thus, express the high mobility of these elements which may subsequently constitute contamination sources for plants and water resources.

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