RESEARCH ARTICLE

CHARACTERIZATION OF FIVE HEAVY METAL FRACTIONS IN AGRICULTURAL SOILS AROUND THE MINE AREA OF DRAA LASFAR, MARRAKECH-MORROCO

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ARTICLE INFO	ABSTRACT
	It is well known that, heavy metals have affinity for different compartment in soil. The risk associated with the presence of metals in soil is their potential ecotoxicity and ability to enter the food chain. Total metal content of a soil is inadequate for predicting the toxicity of heavy metals in soil. Hence, sequential extraction was used in this study to fractionate five heavy metals (Al, Cd, Cu, Pb and Zn) in soils collected from a mining area in order to determine the fraction of the total metal content that is bioavailable. Results showed that aluminium, lead and zinc were mostly associated with long-term mobile fraction (F_3, F_4 and F_5), cadmium was mostly associated with the exchangeable fraction (F_1) while copper was widely abundant in the oxidized form (F_4). The apparent mobility and bioavailability for these five heavy metals in the studied soils were in the order: Cd>Zn>Pb>Cu>Al. This implies that cadmium has the highest mobility in the studied soils.

INTRODUCTION

Environmental pollution by heavy metals originated from functional mines can become a very important source of contamination both in soil and water. Increasing industrial activities and the lack of appropriate measures to counteract its effects are causing a progressive pollution of air, water and soil with heavy metal emissions. Actually, there is increasing awareness that, heavy metals present in soil may have negative consequences on human health and environment (Gleyzes *et al*., 2002, Tessier *et al*., 1979). From environmental point of view, all heavy metals are important because they are non biodegradable and are largely immobile in the soil system. They tend to concentrate and persist especially in soils for a long time (Sahuquillo *et al*., 2003, Aikpokpodion *et al*., 2013). This concentration is caused by the high rate of absorption comparing to the rate of metabolism or excretion of the harmful compounds.

As a result, elevated levels of heavy metals can be found in and around mine areas due to discharge and dispersion of mine wastes into nearby agricultural soils, food crops and stream systems. Eventually, they may pose a potential health risk to residents in the vicinity of mining areas. High mining activity in Marrakech region represents a great hazard due to huge of high amounts of heavy metals. In this concern, few studies have been done in this area to determine the concentration of heavy metals in the mining residues and their impact on surrounding soil and water resources (El Gharmali *et al*. 2004; El Adnani *et al*. 2007; Esshaimi *et al*. 2012). The total heavy metal content in soils provide a convenient means of expressing a measure of pollution but several documented reports have shown that, such measures are inadequate in predicting the toxicity of metal pollutants (Schroeder, 1989). Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways (Rauret *et al*., 1989). The nature of this association is known as speciation. The chemical form of heavy metals in soil is of great significance in determining the potential bioavailability and translocation of the metals to other environmental compartments like water, plant and microorganisms when physicochemical conditions are

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favorable (Fuentes *et al.*, 2004; Wang *et al.*, 2006; Esshaimi *et al.*, 2012). The aim of this study was to determine total heavy metals contents and their chemical fractions in the mining residues and in the samples of soil collected in the vicinity of The Pb-Zn Draa Lasfar mine.

MATERIALS AND METHODS

Site description

Draa Lasfar mine, involves a deposit of pyrite mineral located 10 km northwest of Marrakech city (fig 1) that can pose a risk for the environment due to discharge of tailings all around the mine area (Avila *et al.*, 2012). Draa Lasfar mine is located a few hundred meters from the Tensift River, close to two rural communities (Ouled Bou Aicha and Tazakourte) of about 5790 ha of which 65% are occupied by farmland (Fig 2). The climate is Mediterranean, bordering arid and semi arid with an average annual precipitation of 231 mm (10 years). Temperatures are characterized by great daily and seasonal variation with an average value of 11.5 C° in January and 36.8 C° in July.

Sampling Description

In order to assess the impact of the Draa Lasfar mine on the surrounding environment, a total of 120 samples were collected in the vicinity of the mine covering 230 ha through 8 sampling lines oriented towards specific receptor media (Tensift river creek, Tazakourte village, Ouled bou Aicha village, farms, etc.). 3 representative background samples were taken at the other side of Tensift River at 2 km from the mining site in order to avoid mining contamination. Samples were taken every 50 meters from the upper 20 cm after removing the first layer of surface soil (2 cm) within an area of 100 cm^2. The sampling of the tailings was carried out in 4 tailings reservoirs by using a specially designed cylindrical stainless steel corer, the average sample of each tailings reservoir is considered after mixture of the various subsamples. After collection, the soil and tailing samples were carefully transferred to clean and dry self-sealing polyethylene bags and transported to laboratory. After being air-dried, all samples were sieved through (<2mm or <100 μm) sieve. The tailings samples from each zone were thoroughly mixed and homogenized by coning and quartering. Finally the soil and tailings samples were stored at 4°C in tightly sealed polyethylene bags until its analysis. Due to the strong association and affinity of heavy metals with fine grained soil components, we used the <100 μm soil fraction for the sequential extraction and total acid digestion methods (Cuong and Obbard 2006). The <2 mm soil fraction was used to determine the pH, electrical conductivity (EC), Organic matter content (OM) and carbonate.

Sample analysis

The physical-chemical characterization consisted in the determination of the sample (soils and tailings) pH, electrical conductivity (EC), organic matter content (OM) and the carbonate content according to standard methods (Aubert 1978). Total heavy metal concentration was determined by atomic absorption spectroscopy after digestion of the samples. The methodology followed for the digestion consisted in

weighting 1g dry sample and adding 3 ml HNO3 (70%), 6 ml HCl (37%) and 3 ml HF (48%). The analyzed sample was placed in a sand bath to complete the digestion. After digestion, the sample solution was allowed to air-cool and then diluted with deionized water. The optimized sequential extraction procedure was applied to assess heavy metal fractionation in the samples (Wufem *et al.*, 2013). The sequential extraction was performed using five-step procedure. Additionally, a sixth step was added, which consisted of dissolving the final residue using the same digestion procedure for the total metal determination (Avila *et al.*, 2012).

(F1) Water Soluble: Soil sample extracted with 15 ml of deionized water for 2 hours.

(F2) Exchangeable: The residue from water soluble fraction was extracted with 8 ml of 1M MgCl2 (pH 7.0) for 1 hour.

(F3) Carbonate-Bound: The residue from exchangeable fraction was extracted with 8 ml of IM Ammonium acetate (adjusted to pH 5.0 with Acetic acid) for 5 hours.

(F4) Fe-Mn Oxides-Bound: The residue from carbonate fraction was extracted with 0.04M NH_2 OH. HCl in 25% (v/v) Acetic acid at 96°C with occasional agitation for 6 hours.

(F5) Organic-Bound: The residue from Fe-Mn oxides bound fraction was extracted with 3 ml of 0.02M Nitric acid and 5 ml of 30% HO (adjusted to pH 2 with HNO_3) was added and the mixture heated to 85°C for 3 hours, with occasional agitation.

A second 3 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture heated again to 85°C for 3 hours with intermittent agitation. After cooling, 5 ml of 3.2M NH OAc in 20% (v/v) HNO_3 was added and the samples was made up to 20 ml with deionized water and agitated continuously for 30min.

(F6) Residual: The residue from organic fraction after drying was digested in a conical flask with 10 ml of 7M HNO on a hot plate for 6 hours. After evaporation, 1 ml of 2M HNO3 was added and the residue after dissolution was diluted to 10 ml. the residue was washed with 10 ml of deionized water. After each successive extraction separation was done by centrifuging at 4000 rpm for 30 min. The supernatants were filtered and analyzed for heavy metals.

Quality Assurance: All chemicals used were of reagent grade and pure deionized water was used throughout the experimentation. All plastic ware soaked in 10% HNO_3.

RESULTS

Table 1 shows mean values (%) of the grain-size and geochemical characteristics of different soils and solid tailings of Draa Lasfar mine. These results show that organic carbon of different soils depends on the sand composition of soils. The low organic carbon values of different soils might be related with the poor absorbability of organics on negatively charged quartz grains, which predominate in solid tailings of Draa Lasfar mine. In addition, the constant flushing activity by rain can support the low percentage of organic carbon in these soils.

Table 1. Mean values (%) of the grain-size analysis and geochemical characteristics of different soils and tailings in Draa Lasfar region

	SAB	ST	TDL	Background soil
clay	21,4 ± 2,1	25,3 ± 3,1	1,2 ± 0,3	26,4 ± 2,5
Fine silt	16,1 ± 1,7	16,5 ± 2,7	4,6 ± 1,2	31,6 ± 3,7
Coarse silt	9,2 ± 1,4	8,7 ± 1,5	17,4 ± 1,2	20,1 ± 1,2
Fine sand	25,2 ± 2,9	23,4 ± 3,1	47,4 ± 3,7	5,2 ± 0,7
Coarse sand	27,7 ± 2,5	25,3 ± 2,8	27,4 ± 2,1	5,1 ± 0,4
pH	8,1 ± 0,6	7,8 ± 0,7	2,9 ± 0,2	7,8 ± 0,2
C.E (ms/cm)	1,5 ± 0, 4	1,7 ± 0,4	7,2 ± 0,4	1,0 ± 0,2
CEC (meq/100g)	31,6 ± 3,1	35,2 ± 2,7	7,8 ± 1,6	16,4 ± 1,7
OM (%)	4,7 ± 1,0	5,5 ± 0,7	6,2 ± 1,7	4,3 ± 0,8
OC (%)	2,7 ± 0,6	2,2 ± 0,4	3,6 ± 1,0	1,5 ± 0,3
S %	0,5	0,7	3,7 ± 0,5	1,6 ± 0,4
Cl-	< 0,1	< 0,1	0,7 ± 0,1	< 0,1

Table 2. Mean Concentrations of heavy metals in different soils in Draa Lasfar region

Metals	SAB	ST	TDL	Background soil
Al (mg/kg)	2762,7 ± 1210,0	2877,1 ± 916,4	8504,5 ± 298,8	2433,6 ± 44,1
Cd (mg/kg)	1,1 ± 0,7	2,2 ± 0,2	143,1 ± 11,8	0,2 ± 0,0
Cu (mg/kg)	227,8 ± 225,3	330,5 ± 22,8	928,8 ± 88,5	40,7 ± 0,7
Pb (mg/kg)	184,0 ± 27,1	255,3 ± 24,0	3381,0 ± 507,1	11,8 ± 1,4
Zn (mg/kg)	648,0 ± 174,3	890,5 ± 101,0	2847,8 ± 460,3	133,9 ± 2,0

Results show also that different soils of the studied zone are characterized by slightly basic pH (7.8–8.1) with minimum values recorded in the station closest to the Draa Lasfar mine. These values were different from the low pH values in solid tailings of Draa Lasfar mine which were frequently flooded by the rain and become, in presence of sulfurs, acidic in reducible conditions. Total element concentrations in the investigated soils varied in a narrow range of values (Table 2). This total metal concentration obtained after a strong acid digestion does not provide sufficient information of its potential hazardous effects on environment because the mobility and eco-toxicity of heavy metals depend strongly on their specific chemical forms or binding. Consequently, these are the parameters that have to be determined, rather than the total element contents, in order to assess toxic effects. Heavy metals may be distributed among many components of the soil and may be associated with them in different ways (Aikpokpodion *et al.*, 2013). The nature of this association is known as speciation. The chemical form of heavy metals in soil is of great significance in determining the potential bioavailability and translocation of the metals to other environmental compartments like water, plant and microorganisms when physicochemical conditions are favorable (Cuong *et al.*, 2006).

Aluminium

Figure 3 shows that water Soluble (F1) and exchangeable (F2) fractions exceed 20% of total aluminum in tailings (TDL). These two fractions are fractions of the short-term movable aluminum (F1 and F2) (Sahuquillo *et al.*, 2003). The Carbonate-Bound (F3) and Fe-Mn Oxides-Bound (F4) fractions do not exceed 3% of the total aluminum content, respectively with very low concentration (1, 7 and 1.2% of total metal respectively). This means that aluminum is very weakly bonded organic materials and soil carbonates, but it is somewhat related to the oxides and hydroxides of Fe and Mn (F5). These three fractions constitute the long-term movable aluminum fraction of the (Sahuquillo *et al.*, 2003). The remaining fraction (F6) represents more than 61% of total aluminum making impossible its mobilization. In studied soils,

in the two areas, while the carbonate fraction presents 23 and 20% of the total metal respectively in the SAB and ST soils. The soluble fraction does not exceed 9% of the total metal in the two areas. Draa Lasfar mining effluents carried by the Tensift River (used as irrigation water for agricultural soils in this region) may be responsible for these higher concentrations of non detrital fractions.

Copper

Copper in tailings (figure 5) is essentially bound to soluble (F1) and exchangeable fractions (F2) with more than 32% of the total metal content. Copper is also widely present (31%) in the residual fraction (F6). The oxidizable (F3), acid-soluble (F4) and reducible factions (F5) are represented by small percentages in these tailings; they trap respectively 7, 11 and 13%. Copper presents almost the same distribution in different fractions of studied soils. It is widely abundant respectively in SAB and ST in the oxidized form (29-35%) followed by residual (27-35%) and reducible fractions (19-21%). The soluble and exchangeable fractions poorly represented in these soils. The high percentage of Cu in the residue is likely due to the fact that Cu is easily chemisorbed on or incorporated in clay minerals (Pickering, 1989). The relatively high Cu concentrations in organic phase in the studied soils can be justify by that copper is characterized by high complex constant organic matter thus it can be hypothesized that Cu is bound to labile organic matter such as lipids, proteins, and carbohydrates.

Lead

Lead distribution (figure 6) in tailings is characterized by a strong dominance of this metal bound to long-term mobile fraction (F3, F4 and F5), with more than 61% of the total metal. The short-term mobile fraction (F1 and F2) represents about 18%. The remaining fraction (F6) traps about 27% of the total metal. For studied soils, the lead distribution is the same. Indeed, after the residual fraction, Pb is located, in Carbonate, Fe-Mn oxides and organic fractions. However, the soluble and exchangeable fractions do not exceed 3% in the
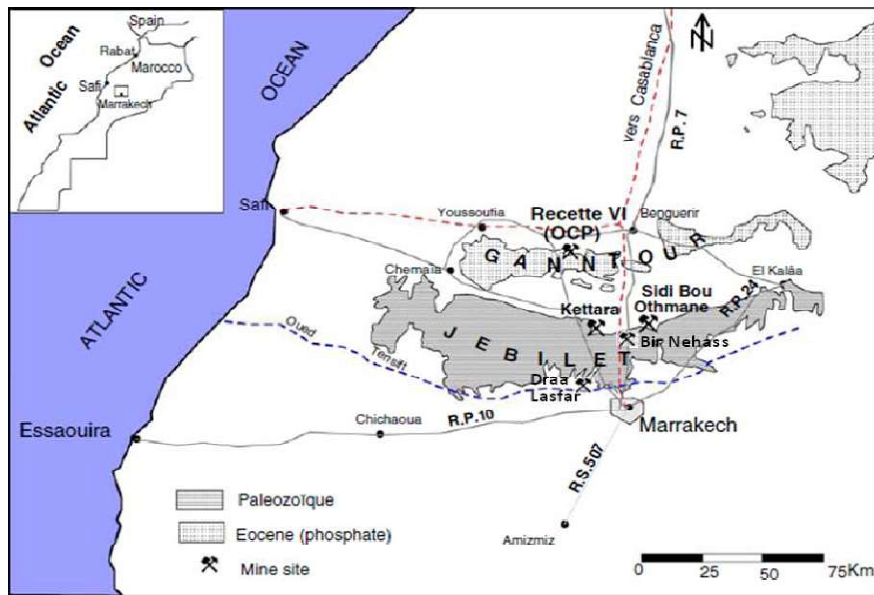
Figure 1. Geographic situation of Draa Lasfar mine in Marrakech region

Figure 2. Geographic situation of Ouled Bouaicha and Tazakourte rural communities
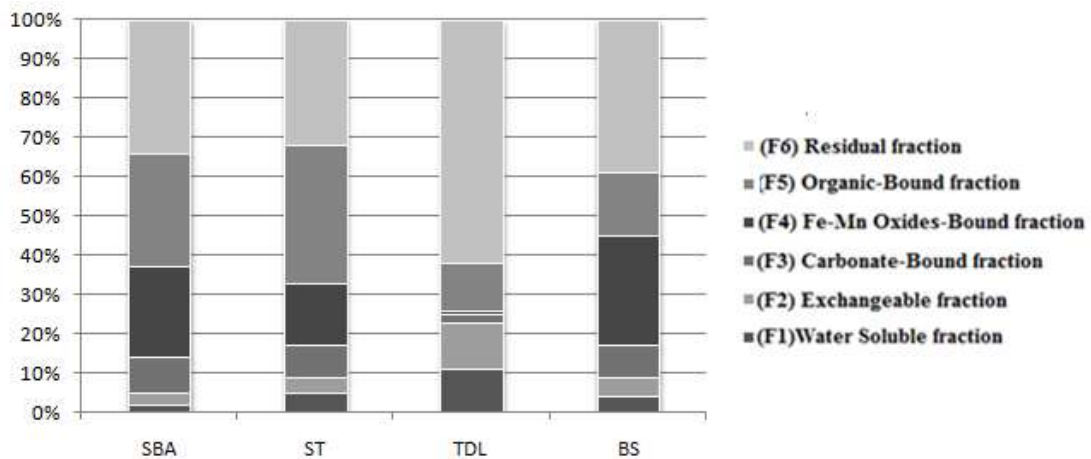

Figure 3. Relative distribution of aluminium among six fractions (F1-F6) of studied samples
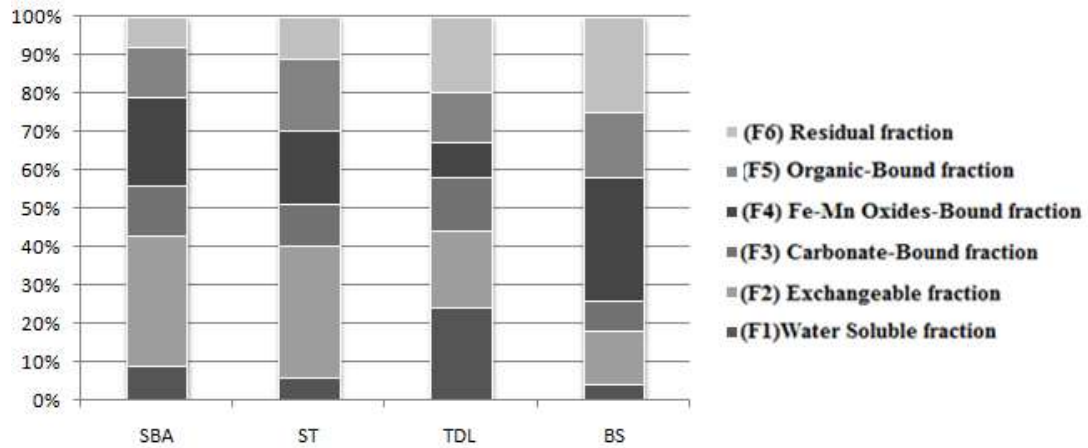
Figure 4. Relative distribution of cadmium among six fractions (F1-F6) of studied samples
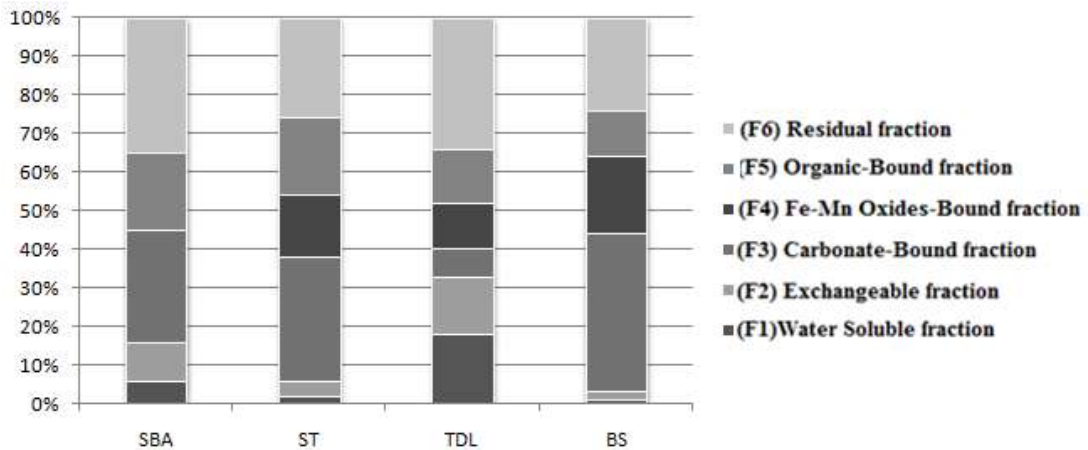

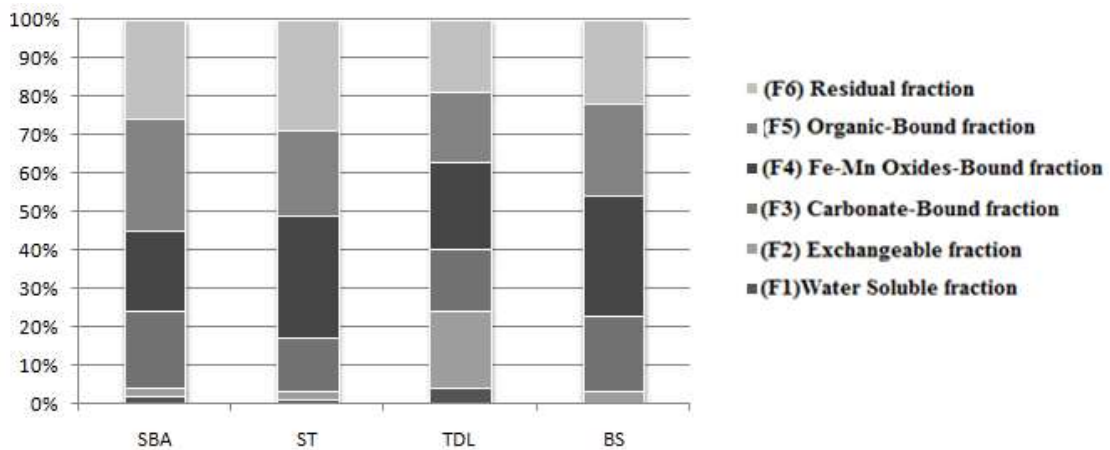**Figure 5. Relative distribution of copper among six fractions (F1-F6) of studied samples**

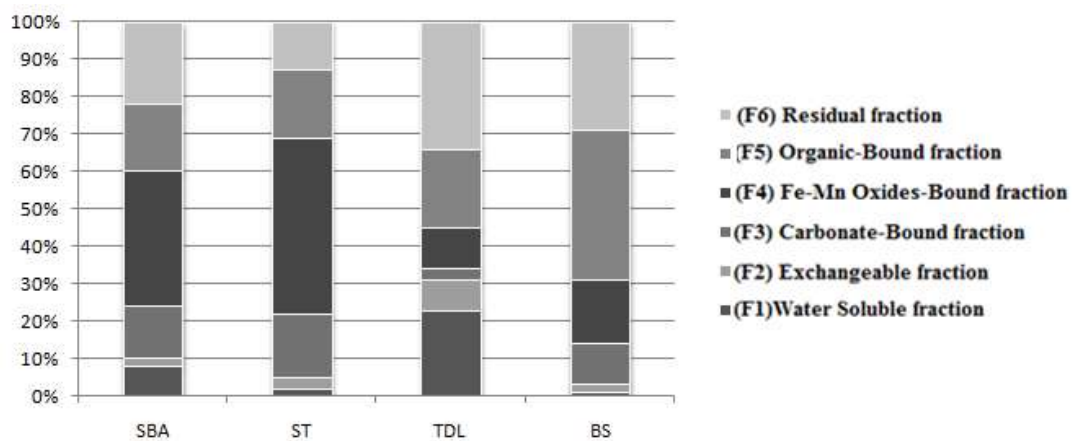**Figure 6. Relative distribution of lead among six fractions (F1-F6) of studied samples**

Figure 7. Relative distribution of zinc among six fractions (F1-F6) of studied samples

two studied areas. The relatively high percentage of Pb in reducible phase is in agreement with the known ability of amorphous Fe–Mn oxides to scavenge Pb from solution (Yusuf, 2007). Thus, a high element percentage in the reducible fraction is a hazard for the aquatic environment because Fe and Mn species can be reduced into the porewaters during early diagenesis by microbially mediated redox reactions (Oluwatosin *et al.*, 2008). Dissolution will also release Pb associated with oxide phases to the porewater possibly to the overlying water column and to benthic biota (Kabala and singh, 2001). The major sources of Pb are from intensive human activities, including agriculture in the drainage basin (Rodriguez *et al.*, 2009). In addition, a substantial contribution from the factories located in the upstream of the Tensift river dealing with Pb play a vital role in soils contamination by heavy metals as referred by Sarkar *et al.*, 2007.

Zinc

Zinc distribution (figure 7) in the tailings shows an equal distribution of this metal in the three fractions with 31% in the short-term fraction (F1 and F2), 34% in the long-term mobile fraction (F3, F4 and F5) and 31% of the total zinc content in the lithogenic fraction (F6). Zinc distribution in the studied soils is almost the same in all soils. Indeed, after the reducible fraction representing between 37 and 48% of total metal, carbonate, organic and residual fractions oscillate between 13 and 21%. The major part of Zn (37 to 48%) is associated with Fe–Mn oxide phase, because of the high stability constants of Zn oxides. Iron oxides adsorb considerable quantities of Zn and these oxides may also occlude Zn in the lattice structures (Banerjee, 2007).

Conclusion

Fractionation of the metals species in soils around the functional Pb-Zn mine shows higher percentages of the metals residing in the non-residual fractions. This suggests potential bioavailability of cadmium, copper, lead, and zinc in the soils around the Draa Lasfar mine, indicative of their anthropogenic source. The knowledge of the chemical speciation of metals in the soil may assist in determining the behaviour of the metals since they occur in different forms in the soil, and may influence their mobility and bioavailabity. The rapidly mobilizable metals in the soil indicate the potential health hazards of cultivated agricultural lands around the mine.

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