

## **Speciation of four heavy metals in agricultural soils around DraaLasfarmine area in Marrakech (Morocco)**

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Received: 21 Nov. 2014

Accepted: 10 Jan. 2015

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**ABSTRACT:** This study was carried out to 1. determine spatial variations of heavy metal deposition in agricultural soils of two rural communities (OuledBouAicha and Tzakourte) of about 5790 ha in a mining area near Marrakech city in Morocco; 2. to assess the extent of metallic pollution generated by the mining activity and; 3. to identify the key mechanism responsible for this contamination and its relation to mining activity. Soil pollution assessment was carried out on one hand by measurement of the total metal concentration and on the other hand by studying four heavy metals speciation of the studied soils. The chemical forms of four heavy metals in soils around DraaLasfar mine were studied by determining soil Cd, Cu, Pb and Zn species using standard solvent extraction and Atomic Absorption Spectrophotometric techniques. The chemical pools of the metals indicated that the metals were distributed into six fractions with most of them residing in the non-residual fractions thus suggesting how readily the metals are released into the environment. Considering that the metals occur in the most available forms, we suggested that it is most likely that the metals must have been derived from anthropogenic sources especially from the mining activity in the studied region.

**Keywords:** heavy metal contamination, mining activity, sequential extraction, soils and tailings, speciation.

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### **INTRODUCTION**

Increasing industrial activities and the lack of appropriate measures to counteract its effects are causing progressive air, water and soil pollution 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 the 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 compared 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 presents a great hazard due to huge discharge of high amounts of heavy metals.

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With regards to this concern, few studies have been carried out 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 their potential bioavailability and translocation to other environmental compartments like water, plant and microorganisms when physicochemical conditions are favorable (Fuentes et al.,

2004; Wang et al., 2006; Esshaimi et al., 2012).

The aim of this study is to determine total heavy metal contents and their chemical fractions in the mining residues and in soil samples collected in the vicinity of the DraaLasfarmine .

## MATERIALS AND METHODS

DraaLasfar 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).

DraaLasfar mine is located a few hundred meters from the Tensift River, close to two rural communities (OuledBouAicha and Tzakourte) 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 variations with an average value of 11.5°C in January and 36.8°C in July.

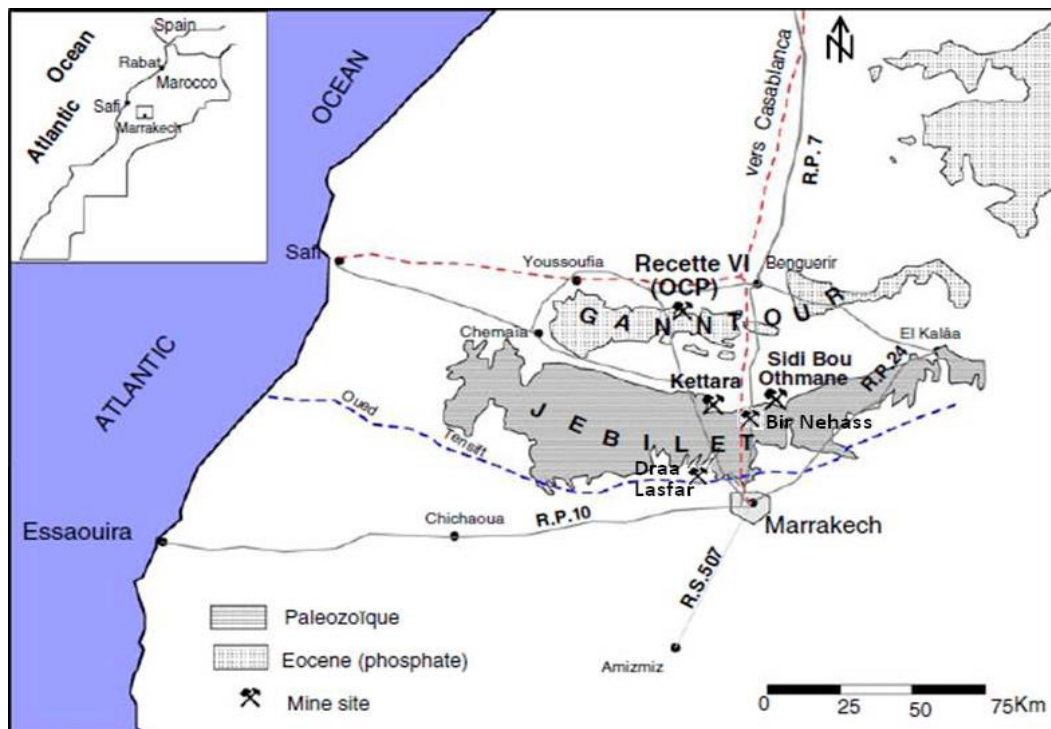


Fig. 1. DrâaLasfar mine geographic situation in Marrakech region



Fig. 2. Geographic situation of OuledBouaicha and Tazakourte rural communities

In order to assess the impact of the DraaLasfar mine on the surrounding environment, a total of 120 soil and tailings 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, Ouledbou Aichavillage, farms, etc.). 3 representative background soil and tailings samples were taken at the other side of Tensift River, 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<sup>2</sup>.

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 the laboratory.

After air-drying, all samples were sieved through a <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 analyses.

Due to the strong association and affinity for heavy metals with fine grained soil components, we used the <100 μm soil fraction in 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.

The physico-chemical characterization consisted of 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 of weighting 1g dry sample and adding 3 ml HNO<sub>3</sub>(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). Sequential extraction was performed using a five-step procedure (F1 to F5). However, a sixth step was added, which consisted of dissolving the final residue using the same digestion procedure for 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 the water soluble fraction was extracted with 8 ml of 1M MgCl<sub>2</sub>(pH 7.0) for 1 hour.

(F3) Carbonate-bound: The residue from exchangeable fraction was extracted with 8 ml of 1M 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<sub>2</sub>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<sub>3</sub>) was added and the mixture heated to 85°C for 3 hours, with occasional agitation. A second 3 ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>) was added and the mixture heated again to 85°C for 3 hours with intermittent agitation.

After cooling, 5 ml of 3.2M NH<sub>4</sub> OAc in 20% (v/v) HNO<sub>3</sub> was added and the samples was made up to 20 ml with deionized water and agitated continuously for 30min.

(F6) Residual: The residue from the organic fraction after drying was digested in a conical flask with 10 ml of 7M HNO<sub>3</sub> on a hot plate for 6 hours. After evaporation, 1 ml of 2M HNO<sub>3</sub> was added

and the residue after dissolution was diluted to 10 ml. the residue was washed with 10 ml 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 experiment. All plastic ware were soaked in 10% HNO<sub>3</sub>.

## **RESULTS AND DISCUSSION**

Table 1 shows estimated mean values (%) of the grain-size and geochemical characteristics of different soils and solid tailings of DraaLasfar Mine.

These results show that organic carbon of different soils depends on their and composition. Low organic carbon values of different soils might be related to poor absorbability of organics on negatively charged quartz grains, which predominate in the solid tailings of DraaLasfar Mine. In addition, the constant flushing activity by rain supports the low percentage of organic carbon in these soils.

The results also show 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 DraaLasfar Mine. These values are different from those in the solid tailings of DraaLasfar Mine which were frequently flooded by rain and became, in the presence of sulphur, acidic in reducible conditions.

Total element concentrations in the investigated soils varied (Table 2). The total metal concentration obtained after strong acid digestion does not provide sufficient information of its potential hazardous effects on the 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.

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

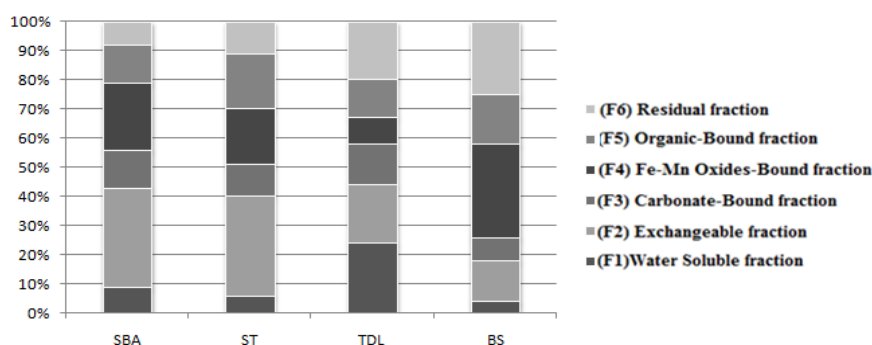
	SBA	ST	TDL	Background soil
clay	21,4 ± 2,1	25,3 ± 3,1	1,2 ± 0,3	26,4 ± 2,5
Fine silt	16,1 ± 1,7	16,5 ± 2,7	4,6 ± 1,2	31,6 ± 3,7
Coarse silt	9,2 ± 1,4	8,7 ± 1,5	17,4 ± 1,2	20,1 ± 1,2
Fine sand	25,2 ± 2,9	23,4 ± 3,1	47,4 ± 3,7	5,2 ± 0,7
Coarse sand	27,7 ± 2,5	25,3 ± 2,8	27,4 ± 2,1	5,1 ± 0,4
pH	8,1 ± 0,6	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 DraaLasfar region

Metals	SBA	ST	TDL	Background soil
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

Heavy metals may be distributed in many soil components 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 their potential bioavailability and translocation to other environmental compartments like water, plant and microorganisms when the physico-chemical conditions are favorable (Cuong et al., 2006).

With the exception of the residual fraction which does not exceed 13% in different soils stations, cadmium presents varied proportions in the other fractions of studied soils. Overall, in solid tailings, cadmium (Fig. 3) seems to be readily available with more than 42% of it bound to the short-term mobile fraction (F1 and F2). The long-term mobile fraction (F3, F4 and F5) contains more than 35% of the total metal. However, the immobilized fraction (F6) finally traps about 20%.



**Fig. 3.** Relative distribution of cadmium among six fractions (F1-F6) of studied samples

In soils, cadmium is mainly present in the labile phase (water soluble, exchangeable and carbonate-bound fractions) with more than 60% in all the stations: The exchangeable fraction represents about 33% of the total metal in the two areas, while the carbonate fraction represents 23 and 20% of the total metal in the SBA and ST soils, respectively. The soluble fraction does not exceed 9% of the total metal in the two areas.

DraaLasfar mining effluents carried by the Tensift River (used as irrigation waters for agricultural soils in this region) may be responsible for these higher concentrations of non-detrital fractions.

In the tailings, copper (Fig. 4) is essentially bound to soluble (F1) and exchangeable fractions (F2) consisting 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 fractions (F5) are represented by 7, 11 and 13%, respectively in the tailings.

Copper shows almost the same

distribution in different fractions of the studied soils. It is widely abundant in SBA and ST in the oxidized form (29-35%) followed by residual (27-35%) and reducible fractions (19-21%). The soluble and exchangeable fractions are poorly represented in these soils.

The high percentage of Cu in the residue is likely due to the fact that it is easily chemisorbed on or incorporated in clay minerals (Pickering, 1989). The relatively high Cu concentrations in the organic phase in the studied soils can be justified by the fact that it 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 distribution (Fig. 5) in tailings is characterized by a strong dominance (61%) of this metal bound to long-term mobile fraction (F3, F4 and F5). The short-term mobile fraction (F1 and F2) represents about 18% while the remaining fraction (F6) consists of about 27% of the total metal.

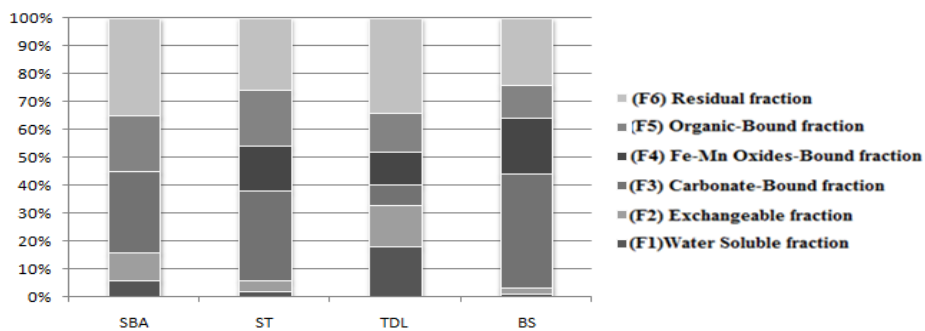


Fig. 4. Relative distribution of copper among six fractions (F1-F6) of studied samples

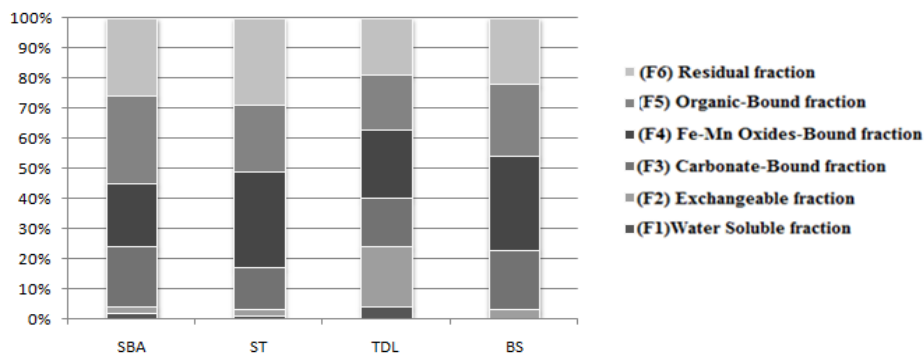


Fig. 5. Relative distribution of lead among six fractions (F1-F6) of studied samples

For the studied soils, lead distribution is the same. Indeed, in the residual fraction, Pb is found in carbonate, Fe-Mn oxides and organic fractions. However, the soluble and exchangeable fractions do not exceed 3% in the two studied areas.

The relatively high percentage of Pb in the 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 hazardous to the aquatic environment because Fe and Mn species can be reduced into the pore waters during early diagenesis by microbially mediated redox reactions (Oluwatosin et al., 2008). Dissolution also

released Pb associated with the oxide phase to the pore water and possibly to the overlying water column and eventually to the 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 soil contamination by heavy metals as noted by Sarkar et al. (2007).

There was equal distribution of zinc in fractions of the tailings with 31% in the short-term fraction (F1 and F2), 34% in the long-term mobile fraction (F3, F4 and F5) and 31% in the lithogenic fraction (F6).

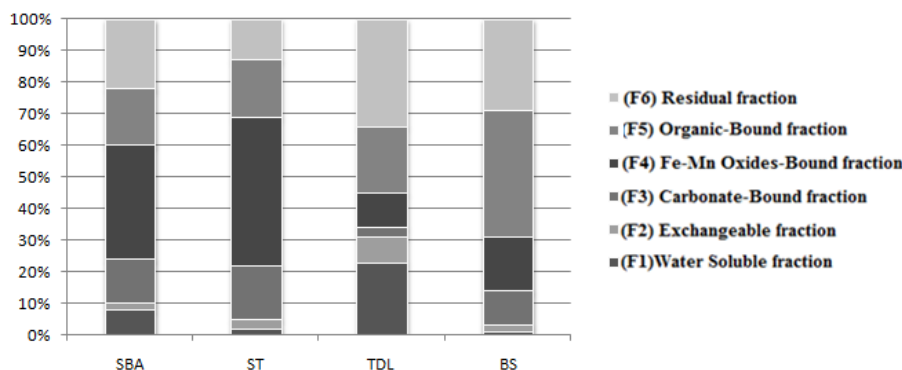


Fig. 6. Relative distribution of zinc among six fractions (F1-F6) of studied samples

Zinc distribution in the studied soils is almost the same as in all soils. Indeed, after the reducible fraction representing between 37 and 48% of the total metal, carbonate, organic and residual fractions fluctuate between 13 and 21%. The Zn component (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

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 it. Hence, sequential extraction was used in this study to fractionate 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. Lead and zinc were mostly associated with long-term mobile fraction (F<sub>3</sub>, F<sub>4</sub> and F<sub>5</sub>), cadmium was mostly associated with the exchangeable fraction (F<sub>1</sub>) while copper was widely abundant in the oxidized form (F<sub>4</sub>). The apparent mobility and bioavailability of these four metals in the studied soils were in the order: Cd>Zn>Pb>Cu. This implies that cadmium has the highest mobility in the studied soils.

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