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Study of potential environmental risk of metallic trace elements in mine tailings: case of Sidi Bou Othmane abandoned mine in Marrakech - Morocco

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Abstract

Environmental pollution by heavy metals originated from functional and or abandoned mines can become a very important source of contamination both in soil and water. Therefore, the characterization of chemical and physical tailings properties is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste. The chemical forms of some heavy metals in tailings of Sidi Bou Othmane mine in north-west of Marrakech city (Morocco) were studied by determining of 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 the metals residing in the non-residual fractions, suggesting how readily the metals are released into the environment. Results showed Cadmium and copper were predominantly associated with short-term mobile fraction (F1 and F2) while lead was largely associated with long-term mobile fraction (F3, F4 and F5) and Zn was essentially bound to Fe–Mn oxide phase (F4). Out of the four studied heavy metals considered in this study, Zn and Pb appeared the most potentially bioavailable indicating its possibility of entering the food chain.

Keywords: mine tailings, metallic trace elements, sequential extraction, mining activity, environmental risk.

Introduction

Industrial processes have been implicated, among many other anthropogenic processes, as a possible source of hazardous metals in the environment. Industrial processes produce particulate emissions [1] even though measures have now been put in place to control these emissions so that there is relatively little dust escaping from closed processing plants in most of such industries [2].

The mining industry is an important asset for the economy of many regions across Morocco, particularly with respect to exports and employment, but also through numerous technological developments.

Active mining operations must respect governmental environmental criteria and, by doing so, the production of contaminants in the environment is limited to a level considered acceptable by the overseeing governments. Nevertheless, some abandoned / functional mine sites are not well controlled and have significant impacts on the environment [3].

Nevertheless, mining operations generate different types of wastes which are potentially environmentally harmful [4, 5].

Mining and milling/beneficiation processes (crushing, grinding, washing,) generate four major categories of waste, i.e. (1) Mine waste (low-grade ore, overburden and barren rocks), (2) Tailings, (3) Dump heap leach and (4) Acid mine water [6]. These wastes loaded with some heavy metals are disposed in surrounding land and water in more or less environmentally acceptable manner.

Mining and milling operations, together with grinding, concentrating ores and disposal of tailings, provide obvious sources of contamination in the surface environment, along with mine and mill waste water (Adriano, 1986). As a result, elevated levels of heavy metals can be found in and around disused metalliferous mines 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 [7, 8].

The goal of this study was to determine the potential for the release of acid and dissolved metals from the Sidi Bou Othmane mine tailings in order to assess the impact of the abandoned mine residues on the surrounding lives' form in this region.

2. Material and methods

2.1 Description of the investigated site

The abandoned Sidi Bou Othmane mine is localized at 30 km in the north-west of Marrakech, in the region of the Haouz district (Jbilets- Centrales) in southern Morocco (figure 1). Sidi Bou Othmane mine is located close to a rural district and surrounded by agricultural lands. Their exploitation started on 1953, treating 115 tons per day of mineral (0.5% Pb, 7.4% Zn and 6% pyrite) by flotation processes until its closure on 1980.

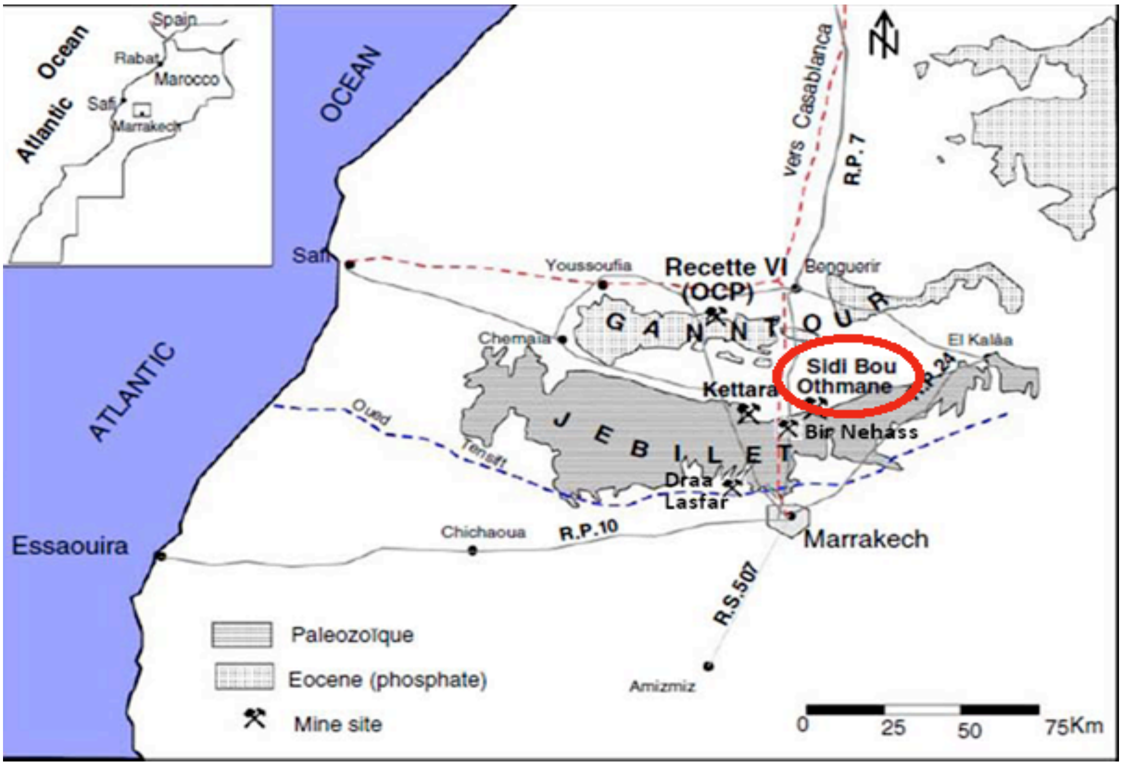

Figure 1: Geographic location of Sidi Bou Othmane mine.

2.2 Sampling Description

The sampling of the tailings was carried out in 5 sampling spots (S1, S2, S3, S4 and S5) of the same tailing reservoir (120m/50m/6m) (figure 2) by using a specially designed cylindrical stainless steel corer, the average sample of each tailing reservoir is considered after mixture of the various subsamples [4, 11, 12, 13].

After collection, the tailing samples were carefully transferred to clean and dry self-sealing polyethylene bags and transported to laboratory. After being air-dried in paper lined propylene trays at room temperature and disaggregated with a wooden roller, all samples were sieved through (<2mm or <100 µm) sieve [4, 11, 12, 13].

The tailings samples from each zone were thoroughly mixed and homogenized by coning and quartering. Finally the 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 tailing fraction for the sequential extraction and total acid digestion methods [7, 9]. The <2 mm tailing fraction was used to determine the pH, electrical conductivity (EC), Organic matter content (OM) and carbonate.

2.3 Sample analysis

The physical-chemical characterization consisted in the determination of the tailings sample pH, electrical conductivity (EC), organic matter content (OM) and the carbonate content according to standard methods.

Total heavy metal concentration was determined by atomic absorption spectroscopy after acid digestion of 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.

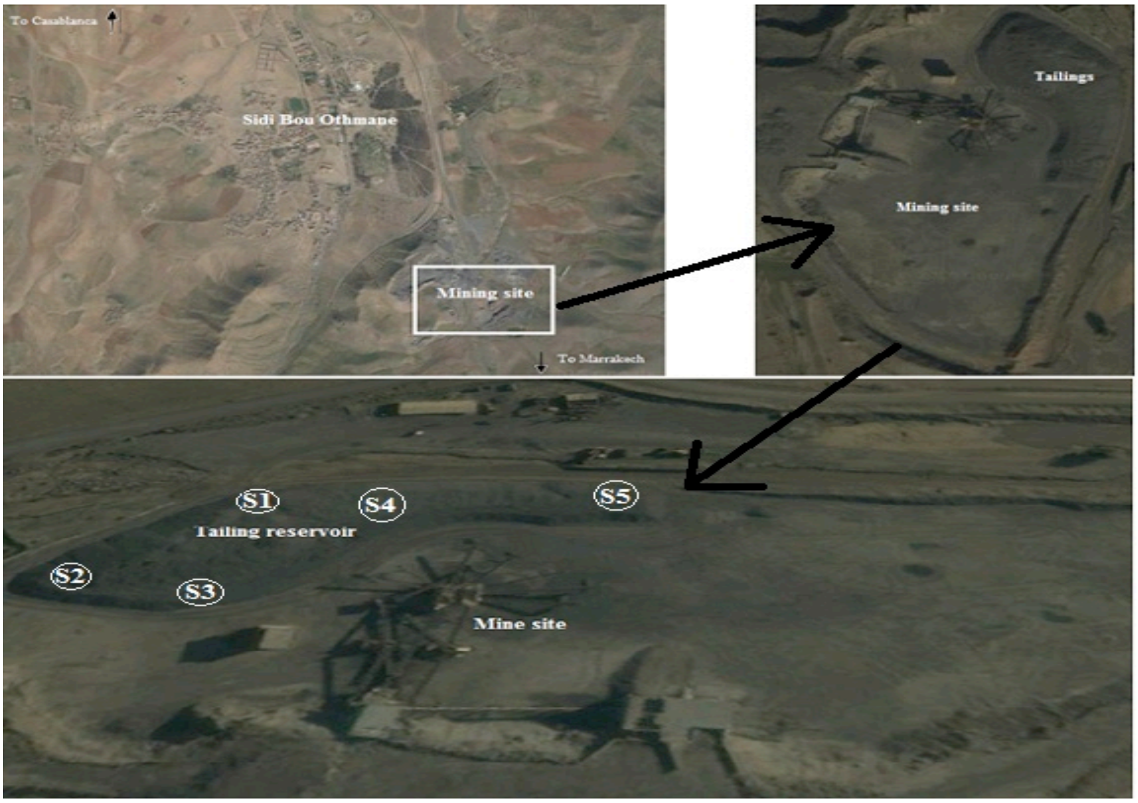

Figure 2: Geographic location and panoramic sight of Sidi Bou Othmane mine tailings.

The optimized sequential extraction procedure was applied to assess heavy metal fractionation in tailings samples [10] . The sequential extraction was performed using five-step procedure [11]. Additionally, a sixth step was added, which consisted of dissolving the final residue using the same digestion procedure for the total metal determination [10, 12].

(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 $MgCl_2$ (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 HNO_3 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.

3. Results and discussion

The results obtained for the tailing grain-size, pH, electrical conductivity (EC), organic matter (OM) and $CaCO_3$ content measurements corresponding to the old Sidi Bou Othmane tailing mine are estimated in table 1.

Table 1: Mean values (%) of the grain-size analysis and geochemical characteristicsof different tailing samples of Sidi Bou Othmane mine.

	S1	S2	S3	S4	S5
clay	26.4 ± 3.1	24.9 ± 3.1	29.1 ± 3.1	26.4 ± 2.5	21.4 ± 2.1
Fine silt	16.7 ± 2.7	17.8 ± 2.7	13.5 ± 2.7	17.6 ± 3.7	16.1 ± 1.7
Coarse silt	9.2 ± 1.5	9.7 ± 1.5	13.8 ± 1.5	17.1 ± 1.2	9.8 ± 1.4
Fine sand	23.4 ± 3.1	22.7 ± 3.1	19.7 ± 3.1	14.2 ± 4.7	25.2 ± 2.9
Coarse sand	24.3 ± 2.8	24.9 ± 2.8	23.9 ± 2.8	25.1 ± 8.4	27.5 ± 2.5
pH	7.4 ± 0.9	7.3 ± 0.7	7.5 ± 0.8	7.1 ± 0.7	7.9 ± 0.6
E.C (μS.cm^{-1})	1539.7 ± 423.8	1757.2 ± 412.8	1846.1 ± 448.2	1236.2 ± 211.4	1589.2 ± 475.6
OM (%)	2.7 ± 1.0	3.5 ± 0.7	3.2 ± 1.7	2.3 ± 0.8	3.7 ± 1.1
OC (%)	2.1 ± 0.6	2.2 ± 0.4	2.6 ± 1.0	1.5 ± 0.3	3.2 ± 1.2
$CaCO_3$(mg.g^{-1})	81.5 ± 17.0	90.4 ± 17.6	82.1 ± 21.4	98.2 ± 12.7	67.9 ± 15.1

These results show that organic carbon (OC) of different tailing samples depends on the sand composition of tailings. 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 Sidi Bou Othmanemine. In addition, the constant flushing activity by rain can support the low percentage of organic carbon in these soils.
Results show also that Sidi Bou Othmane tailings have neutral to alkaline pH for the majority of the samples. Neutral and alkaline pH in mining residues could be attributed to the presence of carbonates with a high concentration ranging from 67.9 to 98.2 mg g-1 for tailings, due primarily to the mixture of these mining residues with soil very rich in carbonates.
The EC measurements reveal that all samples of tailings present a high values ranging from 1236.2 to 1846.1 μS cm^{-1}. Results show also that the most alkaline tailings samples have the lower EC values. This correlation between high pH and low EC value can be explained by the presence of low amounts of sulfur ions that causes a decrease of the EC.
Regarding the carbonate content, it can be stated that tailings with a pH of 7.1 and higher generally have high calcium carbonate content. In this sense, alkaline tailing samples together with high amounts of organic matter and the presence of carbonates increase the retention of heavy metals in these tailing samples [2].
Total heavy metal concentrations in the investigated soils vary 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.

Table 2: Mean total concentrations of heavy metals of different tailing samples of Sidi Bou Othmane mine.

	S1	S2	S3	S4	S5
Cd (mg.kg^{-1})	136.7 ± 17.7	122.2 ± 15.8	143.1 ± 11.8	139.2 ± 20.4	119.7 ± 14.1
Cu (mg.kg^{-1})	947.8 ± 65.3	930.5 ± 42.8	928.8 ± 88.5	870.7 ± 45.7	945.7 ± 35.2
Pb (mg.kg^{-1})	3184.0 ± 27.1	3255.3 ± 24.0	3381.0 ± 57.1	3211.8 ± 61.4	2911.8 ± 71.4
Zn (mg.kg^{-1})	3648.0 ± 174.3	2890.5 ± 101.8	2847.8 ± 60.3	3133.9 ± 112.4	2733.9 ± 78.4

Heavy metals may be distributed among many components of the tailings and may be associated with them in different ways [4]. The nature of this association is known as speciation.

The chemical form of heavy metals in tailing components is of great significance in determining the potential bioavailability and translocation of the metals to other environmental compartments like water, soil, plant and microorganisms when physicochemical conditions are favorable [13].
With the exception of the residual fraction which does not exceed 16% in different samples, cadmium presents varied proportions in the other fractions of studied tailings.
Overall, cadmium in all tailing samples (figure 3) seems to be very available with more than 46 to 57% of total metal and appears to be bound to the short-term mobile fraction (F1 and F2). The long-term mobile fraction (F3, F4 and F5) homes more than 28 to 36% of total metal. However, the immobilized fraction (F6) finally traps about 9 to 16%.

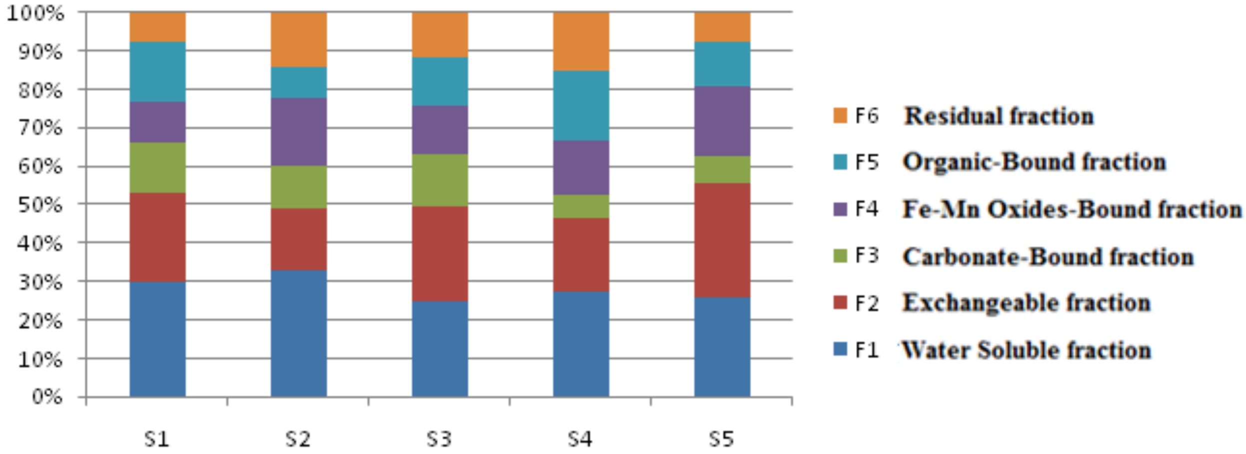

Figure 3: Relative distribution of cadmium among six fractions (F1-F6) of studied tailing samples.

Copper in tailings (figure 4) is essentially bound to soluble (F1) and exchangeable (F2) fractions with more than 33 to 47% of this total metal content. Copper is also widely present (24 to 30%) 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 about 4 to 7, 10 to 14 and 12 to 14%.

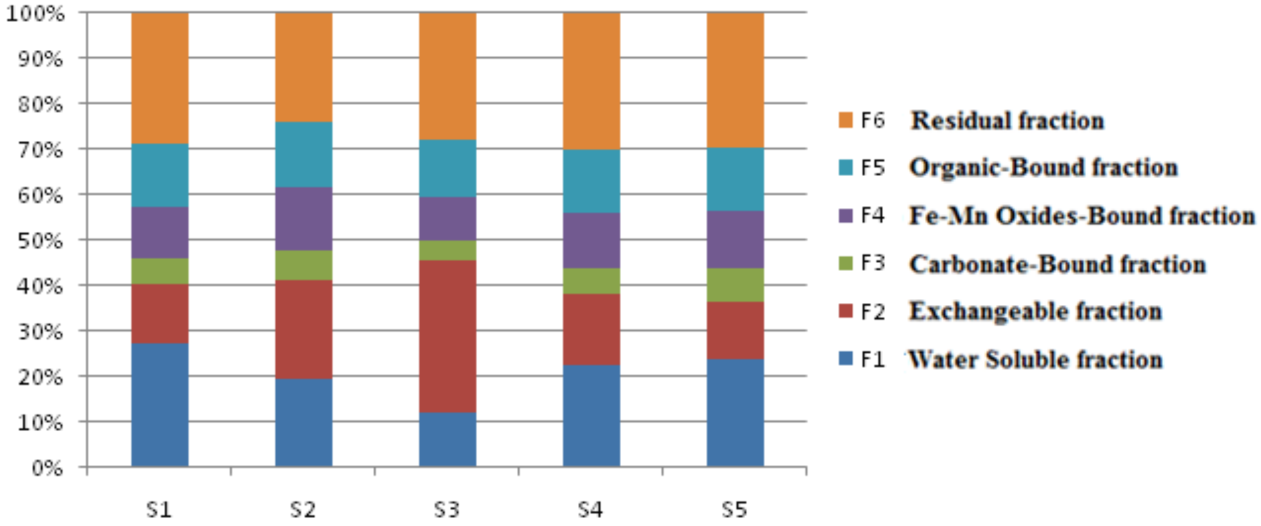

Figure 4: Relative distribution of copper among six fractions (F1-F6) of studied tailing samples.

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 [9]. The relatively high Cu concentration in organic phase in the studied samples 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 [16].

Lead distribution (figure 5) in tailings is characterized by a strong dominance of this metal bound to long-term mobile fraction (F3, F4 and F5), with more than 47 to 54% of this total metal. The short-term mobile fraction (F1 and F2) represents about 19 to 26%. The remaining fraction (F6) traps about 17 to 22% of this total metal.
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 [14]. 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 pore waters during early diagenesis by microbially mediated redox reactions [15]. Dissolution will also release Pb associated with oxide phases to the porewater possibly to the overlying water column and to benthic biota [16]. The major sources of Pb are from intensive human activities, including agriculture in the drainage basin [17]. 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 [18].
Zinc in tailings (figure 6) is essentially bound to Fe–Mn oxide phase (F4) with more than 37 to 48% of this total metal content. This result can be justified by 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 [19]. Zinc is also widely present (27 to 33%) in the residual fraction (F6). The water soluble (F1) and exchangeable (F2) fractions are represented by relatively small percentages in these tailings; they trap respectively about 8 to 13% and 7 to 12%. The impact of these heavy metals on the environment and specially on water was widely discussed [20-22].

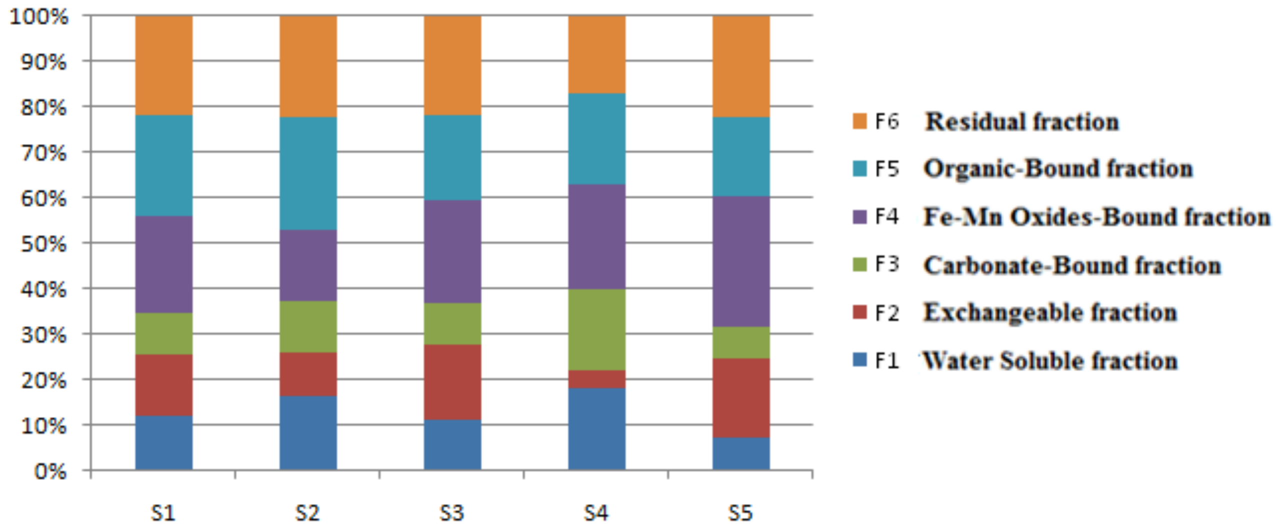

Figure 5: Relative distribution of lead among six fractions (F1-F6) of studied tailing samples.

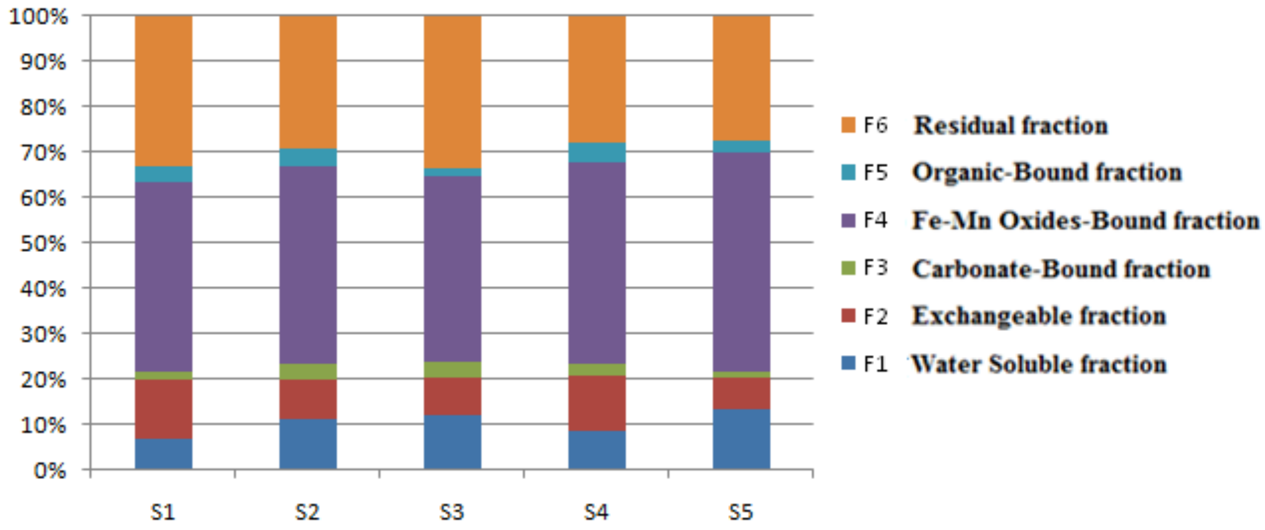

Figure 6: Relative distribution of zinc among six fractions (F1-F6) of studied tailing samples.

Conclusion

Environmental pollution by heavy metals originated from abandoned mines can become a very important source of contamination both in soil and water. Therefore, the characterization of chemical and physical properties tailings is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste. Taking into consideration the high mobility and potential bioavailability of heavy metals in this fraction and their total concentration, it can be concluded that Sidi Bou Othmane mine tailings could have potentially hazardous effects on the environment.

Cadmium and copper were predominantly associated with short-term mobile fraction (F1 and F2) while lead was largely associated with long-term mobile fraction (F3, F4 and F5) and Zn was essentially bound to Fe–Mn oxide phase (F4). Out of the four studied heavy metals considered in this study, Zn and Pb appeared the most potentially bioavailable indicating its possibility of entering the food chain.

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