Pollution, 2(1): 93-101 , Winter 2016
DOI: 10.7508/pj.2016.01.010
Print ISSN 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir Email: jpoll@ut.ac.ir

Contamination by trace elements of agricultural soils around Sidi Bou Othmane in abandoned mine tailings in Marrakech, Morocco

Yassir, B. [1,2*]**, Sana**[3]**, E.F., and Alain, P.**[1]

1. Laboratoire de Toxicologie et d'hygiène Industrielle, 1 rue Gaston Veil, 44035, Nantes Cedex, France
2. Laboratoire Régional du diagnostic épidémiologique et d'hygiène du milieu, Avenue des hôpitaux, Marrakech, Maroc
3. Département de Biologie, Faculté des Sciences Semlalia, Bd Moulay Abdellah Bp, 2390-40001, Marrakech, Maroc

Received: 7 Aug. 2015 Accepted: 10 Sep. 2015

ABSTRACT: This study was carried out for the purpose of investigating the issue of tailings dams as a potential source of contamination by trace elements in soils at the Sidi Bou Othmane mine in the Marrakech Region, Morocco. Soil samples taken from depths of up to 15 cm and within a radius of 50 m from the tailings dams, were analyzed for Cd, Cu, Pb and Zn using atomic absorption spectrometry. Average concentrations of Cd, Cu, Pb and Zn in soils around the abandoned tailings dams were, respectively, 157.2±8.8, 969.1±38.7, 1640.7±42.7 and 2846.8±84.6 mg/kg. Soils in the vicinity of the decommissioned tailings dams registered increased values for Cd, Cu, Pb and Zn. Contamination factors (CF) and pollution index (PI) were calculated in order to estimate the anthropogenic contribution of target pollutants which determined Cd, Cu, Pb and Zn as the main pollutants in this region. The results revealed the polluted areas in the vicinity of the mine, especially two rural communities apparently linked to the lack of appropriate measures to counteract the effects of these mine tailings, which were causing a progressive contamination of the soil with residues of heavy metal emissions in this region under study. Improved strategies for the management of tailings, among other factors, might have influenced the reduced level of contamination by trace elements at the abandoned mine tailings dam sites.

Keywords: contamination, heavy metals, mine area, mine tailings, Marrakech, soils

INTRODUCTION

With global changes presenting new challenges in environmental protection and conservation, there is need for baseline data to help evaluate the potential impacts of pollutants on ecosystems. Activities, such as mining for metals, release large quantities of tailings and waste containing heavy metals which pose a severe threat to water resources, agricultural soils and food crops (Avila *et al.*, 2013).

Mining, no doubt, has a negative impact on agriculture because of the complex catena of various interactions that occur as waste material becomes part of the ecosystem into which it is deposited. Mining activities have been reported to have impacts, such as oxidation of metal sulfides, which induces soil acidification, impeding natural colonization of vegetation, thus causing soil erosion and degradation of the aquatic ecosystem leading to destruction of aquatic life. To further compound this situatiuon, acidic

[*] Corresponding Author: yassirbark@yahoo.fr

mine water impacts on agricultural lands that are irrigated with it.

Environmental pollution, especially by chemicals, is one of the most effective factors in the destruction of biosphere components (Barkouch *et al*., 2015). Among all chemical components, potentially toxic metals (PTM) are believed to be of specific ecological, biological and health significance.

In soils, their forms are strongly determined by their origin and history (Avila *et al*., 2013). Although native metals are frequently found in highly immobile forms, anthropogenic forms are often more reactive, and thus, are more readily available to plants (El Hamiani *et al*., 2015). Soil is a dynamic system, and any changes in environmental conditions, whether natural or anthropogenic, can alter the forms of PTMs, thereby affecting their behavior in the soil. The main controlling factors include degradation of organic compounds, change of soil pH, redox potential and ionic strength of the soil solution, as components of solids and solutions, and their relative concentrations and affinities for an element, and time (Alloway, 1995; Jung *et al*., 2002; Liu *et al*., 2003; Tahiri *et al*., 2005, Favas *et al*., 2011).

The term, PTM, includes essential (e.g., Cu, Mn, Se, Zn, Co) and nonessential (e.g., As, Hg, Cd, Pb) elements. The elements essential to healthy functioning and reproduction of microorganism, plants and animals are required in low concentrations. While these are also called micronutrients, at high concentrations they may cause direct toxicity or reproductive side effects in plants, animals and humans (Bolan and Duraisamy, 2003; Esshaimi at al., 2013). Some elements are also nonessential, and even low concentrations of such elements in the environment can cause toxicity to both plants and animals (Alloway, 1995).

PTMs contamination is widespread, as they are nonbiodegradable and, therefore, persist for long periods in aquatic as well as terrestrial environments (Kabata-Pendias and Pendias, 2001). It is generally accepted that the distribution, mobility, bioavailability and toxicity of PTMs in soil depend, not simply on their total concentrations, but critically, on their forms (Morgan and Stumm, 1995). These may be soluble, readily exchangeable, complexed with organic matter, or hydrous oxides, substituted in stoichiometric compounds, or occluded in mineral structures (Ritchie and Sposito, 2002; Favas *et al*., 2011).

The main objective of this work was to characterize, physically and chemically, the wastes and soils taken from the Sidi Bou Othmane mining areas, in order to assess the main pollutants, their levels of contamination, their distribution among different particle size fractions, and their mobility/bioavailability as assessed by sequential extraction.

This paper concludes by studying wind transport of dust to be an important factor influencing the spreading of heavy metal contamination of agricultural soils in this zone.

This study will contribute to awareness of the potential impacts of pollutants, and hopefully provide a key to effective management of surface soil quality in this mining area.

MATERIAL AND METHODS

Description of the investigated site

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

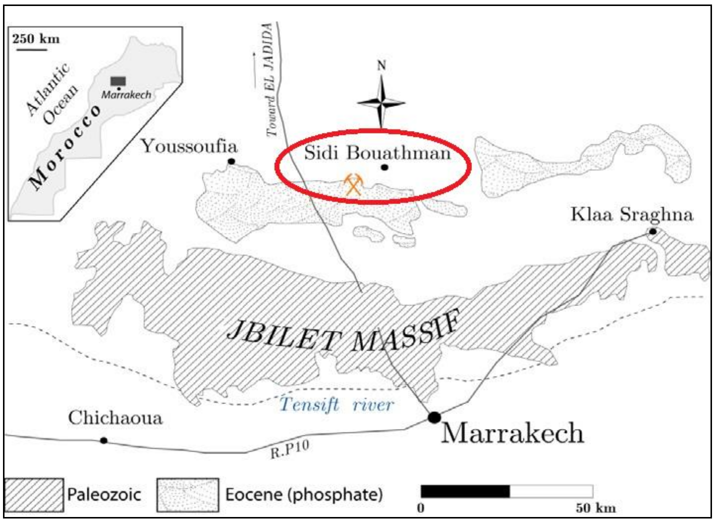

Fig. 1. Geographic location of the Sidi Bou Othmane mine

Sampling Description

In order to assess the impact of the Sidi Bou Othmane mine on the surrounding environment, a total of 90 samples were collected in the vicinity of the mine covering 860 ha (Fig. 2). Six other samples were taken at a distance of 3 km from the mining site as background soils, in order to avoid mining contamination.

Soil samples analysis

Soil samples from the various sampling sites (Sidi Bou Othmane rural center = RC, Sidi Bou Othmane agricultural soils= AS and Sidi Bou Othmane mine tailings= MT) were all taken at depths of 0–20 cm each with the help of a garden shovel cleaned with concentrated nitric acid (Fig. 3). Five samples were taken from each sampling site over the course of 6 months between 2014 and 2015. The soil samples were collected in plastic containers which had all been precleaned with concentrated nitric acid. This was done to remove any traces of heavy metal contaminants (Brigden *et al*., 2008).

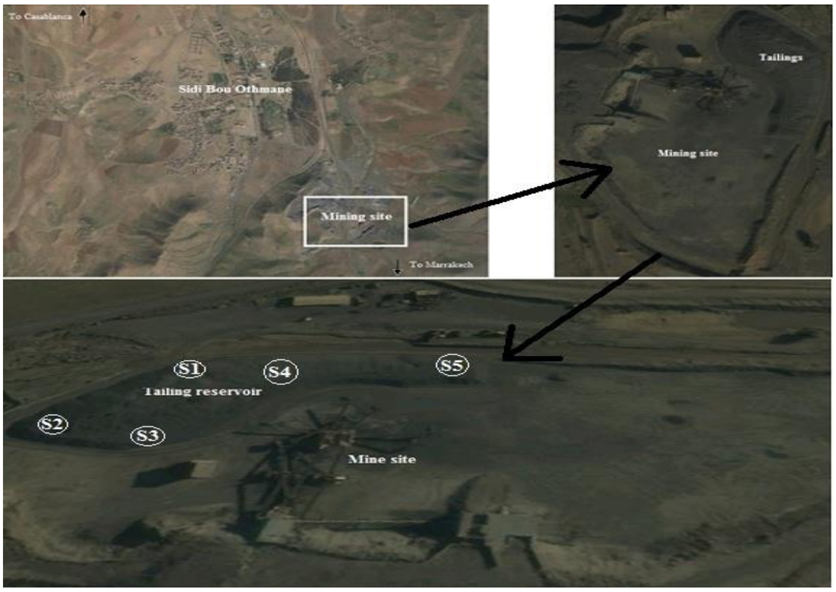

Fig. 2. Geographic location and panoramic sight of Sidi Bou Othmane mine tailings

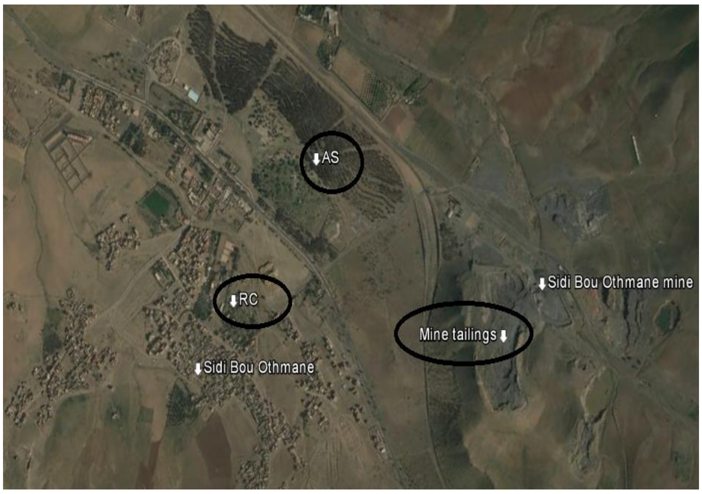

Fig. 3. Geographic locations of the Sidi Bou Othmane mine tailings, RC and AS

All samples were dried and passed through a 2 mm sieve. Aliquots of about 1 g were digested with 5 ml 65% HNO_3 in a microwave digestion system for the determination of the HNO_3-soluble fraction of heavy metals. The concentrations of Cd, Cu, Pb and Zn were determined by means of a graphite furnace atomic absorption.

Soil pH was measured in soil-H_2O suspension (1:2.5, w/w), and electrical conductivity was measured in a 1:5 soil to water suspension using an HI 9828 multiparameter portable (HANNA instruments). Organic matter content was determined by the Walkley and Black procedure (Nelson and Sommers, 1982).

Soil samples were dried at 60°C for 75 hours; then each sample was crushed, sieved (<325 µm), homogenized, and weighed. Soil particle size distribution was measured using the hydrometer method (Allen *et al*., 1974).

Carbonate content was determined following the methodology of Horton and Newson (1953).

RESULTS AND DISCUSSION

Textural characteristics of the soils studied are shown (Table 1) according to the classification of Shepard (Shepard and Moore, 1954). These results showed that clay (≤0.002 mm) and coarse silt (0.02–0.063 mm) were dominant fractions of all Sidi Bou Othmane soil samples, with a range from 24.9 to 26.7%, and 21.7 to 22.9% in RC and AS, respectively. Fine silt (0.002–0.0063 mm) is represented from 19.8 to 22.7% in RC and AS, respectively.

pH, EC and carbonate ($CaCO_3$) content are geochemical soil characteristics that are able to provide sufficient information to understand a soil's capacity to retain heavy metal pollutants (De Matos *et al*., 2001). Numerical values of pH, EC and $CaCO_3$ for each analyzed sample can be found in Table 2.

Table 1. Mean values (%) of the grain-size analysis of different soils in the Sidi Bou Othmane region.

	RC	AS	MT	Background soil
clay	24.9±3.2	26.7±4.4	26.4±2.5	15.4±2.5
Fine silt	19.8±2.7	22.7±2.1	17.6±3.7	19.6±3.7
Coarse silt	21.7±1.2	22.9±2.1	17.1±1.2	11.1±1.2
Fine sand	11.1±3.4	13.9±3.4	14.2±4.7	25.2±1.7
Coarse sand	15.7±3.5	14.3±3.8	25.1±8.4	21.1±1.4

Results obtained for the soil pH measurements revealed that, in general, all sampled points presented a slightly acidic to neutral pH ranging from 6.3 to 7.2, lower than the background soil, with the exception of a very acidic sample corresponding to the tailing sample with a pH 5.1.

These variations in soil pH seemed to be related to heterogenous deposits of sulfidic residues generated by mine tailings at the surroundings of the studied mine, which can cause a reduction in pH by corresponding oxidation and formation of sulfuric acid (0.7–1.3% of S).

Table 2. Geochemical characteristics of different soils in the Sidi Bou Othmane region

Parameters	RC	AS	MTK	Background soil
pH	7.2±0.3	6.3±0.3	5.1±0.5	7.8±0.2
E.C ($\mu S.cm^{-1}$)	1849.4±137.4	2048.5±124.1	6478.9±164.2	958.4±82.1
OM (%)	4.1±1.0	5.2±0.7	3.2±1.7	2.3±0.8
OCC (%)	2.7±0.6	3.2±0.4	2.6±1.0	2.9±0.5
$CaCO_3$ ($mg.g^{-1}$)	158.7±32.4	124.8±27.8	162.1±21.4	134.9±17.4
S %	0.7	1.3	4.2	0.3
Cl-	< 0.1	< 0.1	< 0.1	< 0.1

EC showed more variability than the pH, with values ranging from 1849.4 to 2048.5 μS/cm. These obtained values of EC are significantly higher than for the background samples which indicate an increasing salinity gradient and, consequently, high amounts of labile ions close to the mine area. Mine tailings constitute a hot spot with an EC of 6478.9 μS/cm. This high value is mainly due to the high volumes of metals present in this area.

Among the factors influencing the accumulation of metals, particle size played a significant role. Fine grained soils often show higher concentrations of nutrients due to their greater surface-to-volume ratio, and enrichment of organic matter (OM) (Wang *et al*., 2004).

Mean organic matter contents in the soils that were studied were in the range of 4.1 in RC and 5.2% dw in AS. These results can be justified by the anthropogenic contribution by the discharge of domestic sewage at the Sidi Bou Othmane region, which was an important source of OM at this mining zone. High values of organic content were due to agricultural activities in the vicinity of the mine in AS.

The organic carbon content (OCC) ranged from 2.7% dw in RC to 3.9% dw in AS.

This parameter increased in the soils of AS, corresponding to a decrease in the soil grain size. The highest organic carbon contents were found in the soils that had the lowest sand content and the highest silt and clay contents (Table 1).

Table 3 shows the estimated results of total concentrations for the elements Cd, Cu, Pb and Zn in soils. All the results are expressed in mg/kg.

The concentrations of heavy metals were higher in the soils of AS than in those of RC. Heavy metal concentrations in these soils are strongly determined by local geology or anthropogenic influences. The weathering of minerals is one of the major natural sources, while anthropogenic sources include use of fertilizers and herbicides, irrigation and industrial effluents. In this agricultural area, the Sidi Bou Othmane abandoned mine tailings are likely to be the major source of contamination.

Table 3. Mean concentrations of heavy metals in different soils in the Sidi Bou Othmane region.

Metals	RC	AS	MTK	Background soil	maximum tolerable (a)
Cd (mg/kg)	2.1 ± 0.2	2.6 ± 0.7	157.2 ± 8.8	0.4 ± 0.1	1.5
Cu (mg/kg)	423.5 ± 21.8	527.8 ± 25.3	969.1 ± 38.7	40.7 ± 0.7	300
Pb (mg/kg)	278.5 ± 24.0	321.7 ± 27.1	1640.7 ± 42.7	11.8 ± 1.4	150
Zn (mg/kg)	672.1 ± 35.7	723.4 ± 74.3	2846.8 ± 84.6	133.9 ± 2.0	300

(a) Maximum allowable concentrations of heavy metals for agricultural soils established in the European Directive 86/278/EEC (Council of the European Communities 1986).

Total metal concentrations were classified based on the background levels for sandy soils (Kabata-Pendias and Pendias, 2001), and the upper values established by European Directive 86/278/EEC (Council of the European Communities 1986) (Table 3). Values of total Pb, Zn, Cd and Cu concentrations in the samples of soils and tailings (determined after acid digestion), are shown in Table 3. As expected, in most of the mines, the tailings had higher metal concentrations than the soil. The tailings from this abandoned mine contained very high levels of Cd (157.2 ± 8.8 mg kg^{-1}), Cu (969.1 ± 38.7 mg kg^{-1}), Pb (1640.7 ± 42.7 mg kg^{-1}) and Zn (2846,8 ± 84.6 mg kg^{-1}).

The adjacent soils were also highly contaminated with metals (Zn, Pb, Cu, Cd), according to the classification of the upper values established by the European Directive 86/278/EEC (Council of the European Communities 1986). The soils taken near the area covered by tailings showed the highest values for all the metals (RC and AS). This finding corroborates the findings of Esshaimi *et al*. (2013), who found that almost all these soil samples were classified into very polluted levels (Council of the European Communities 1986) for Zn, Pb, Cu and Cd (values particularly high for Zn and Pb).

All the heavy metal values determined were above the maximum values allowed in the directives (Council of the European Communities 1986) (Table 3). It is very important to consider that these elements (particularly Zn and Pb) have high toxicity, which fact suggests the common origin of all the metals analyzed and, therefore, the mining activity can be pointed out to be the source for the metal pollution of the area under study. Two reasons may be suggested to explain the scattering of the metals from the mine area. Firstly, the mining residues had higher metal concentrations, particularly Zn and Pb (Table 4). This fact is probably due to the postprocessing of the mine tailings, which were crushed, ground and treated by flotation. This process would have recovered the small amounts of ore minerals (e.g., galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS2)), remaining in the tailings from the original works, (the processing was designed to handle a capacity of 115 tons per day (7.4% Zn 0.5% Pb, and 6% pyrite) using the flotation process). Secondly, wind transport of dust may be another important factor influencing the spreading of pollution.

The results also showed significant spatial variations. Compared to the background soil and the contents of other heavy metals, the soils studied showed a significant increase. The highest levels were observed in AS. The study of the wind rose of Sidi Bou Othmane region can be used to justify the increase of concentrations of traces of metallic elements obtained in AS.

Strictly defined, the wind rose denotes a class of diagrams designed to display the distribution of wind direction experienced at a given location over a period of time.

The wind rose (Fig. 4) showed that west-southwest wind directions are dominant, and that the relative frequency of the wind speed covers the samples site of AS, which explains the role of wind as a principal transportation and dispersion factor of metallic elements in this region.

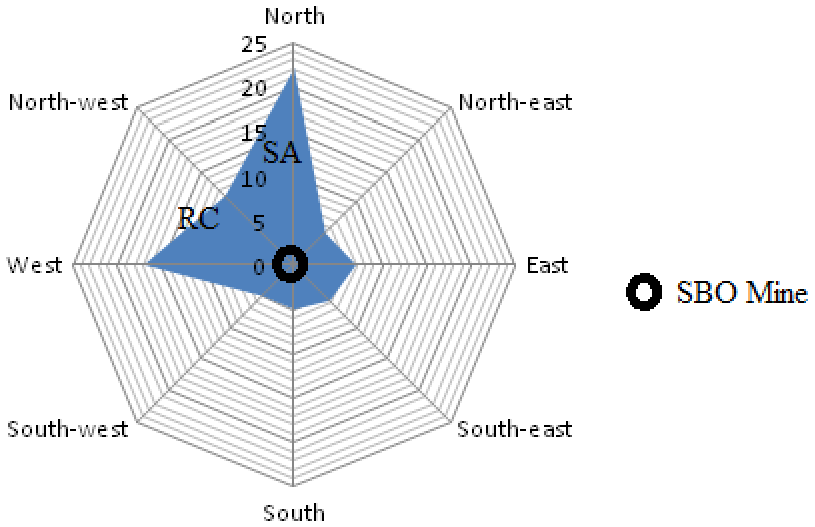

Fig. 4. Wind rose of the Sidi Bou Othmane mine district

The calculated contamination factors (CF) (Table 4) serve to show the extent of this increase in metallic contamination. The pollution index (PI) is the arithmetic mean of the CF of analyzed metals (Gonçalves *et al.*, 1992, 1994; Sanchez *et al.*, 1994), and it allows an assessment of the degree of polymetallic pollution of analyzed soil samples. With a value greater than 1, it is an indication that the analyzed sample had a metallic contamination caused by human activities.

Table 4. Contamination factors and PI of different soils in Sidi Bou Othmane region

		Soil samples		
	Eléments	**RC**	**AS**	**MT**
Contamination factors	Cd	5.3	6.5	393
	Cu	10.4	13.0	23.8
	Pb	23.6	27.3	139.0
	Zn	5.0	5.4	21.3
Pollution Index		**44.3**	**52.1**	**577.1**

The PI (Table 4) showed that AS and RC soils have a high metal contamination because their PIs are well above the legal limit of pollution that is equal to 1. In addition, AS and RC are clearly highly polluted, as their respective PIs (52.1 and 44.3) are high (Table 4).

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 the chemical and physical properties of tailings is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste. The chemical characteristics of agricultural soils in the vicinity of the abandoned mine of Sidi Bou Othmane showed that, in general, all samples presented a weakly acidic to neutral pH. The characterization also revealed that all the soil samples presented a very high organic matter content compared to the background samples. These values are due to agricultural activities in the vicinity of the mine. The total heavy metal concentrations showed that the highest concentrations were Pb and Cu, and the total concentrations were above the maximum allowable concentrations of heavy metals for agricultural soils stipulated in the European Directive 86/278/EEC.

This study concludes that wind transport of dust may be an important factor influencing the spreading of pollution of soils in this region.

REFERENCES

Allen, S.E., Grimshaw, H.M., Parkinson, H. M. & Quarmby, J.A. (1974). Chemical Analysis of Ecological Materials. Blackwell Scientific publications, Oxford.

Alloway, B.J. (1995). The origins of heavy metals in soils. In: Alloway B.J. (Ed.), Heavy Metals in Soils. Blackie Academic and Professional Publ., New York. 368 pp.

Avila, M., Perez, G., Esshaimi, M., Mandi, L., Ouazzani, N., Brianso, J.L. and Valiente, M. (2013), Heavy Metal Contamination and Mobility at the Mine Area of Draa Lasfar (Morocco). Open Environ. Pollut. Toxicol. J, 3(1) 2-12

Barkouch, Y., El Fadeli, S., Khadiri, M. and Pineau, A. (2015), Study of potential environmental risk of trace metallic elements in mine tailings: Case of Draa Lasfar functional mine in Marrakech – Morocco. Afr. J. Agri. Res, 10(33), 3246-3252.

Bolan, N.S. and Duraisamy, V.P. (2003). Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res., 41, 533-555.

Brigden, K., Labunska, I., Santillo, D. and Johnston, P. (2008). Chemical contamination at e-waste recycling and disposal sites in Accra and Korforidua, Ghana. Greenpeace Research Laboratories Technical Note. Greenpeace International, Amsterdam, The Netherlands.

Council of the European Communities, (1986). Directive (86/278/EEC) on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities, L181, 6–12.

De Matos, A.T., Fontes, M.P.F., Da Costa, L.M. and Martínez, M.A. (2001) Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. Environ. Pollut., 111, 429-35.

El Hamiani, O., El Khalil, H., Sirguey, C.,Ouhammou, A., Bitton, G., Schwartz, C. and Boularbahh, A. (2015), Metal Concentrations in Plants from Mining Areas in South Morocco: Health Risks Assessment of Consumption of Edible and Aromatic Plants, CLEAN Soil, Air, Water, 43 (3), 399–407.

Esshaimi, M., Ouazzani, N., El Gharmali, A., Berrekhis, F., Valiente, M. and Mandi, L. (2013), Speciation of Heavy Metals in the Soil and the Tailings, in the Zinc-Lead Sidi Bou Othmane Abandoned Mine. J. Environ. Earth. Sc, 3(8), 138-146.

Favas, P.J.C., Pratas, J., Elisa, M., Gomes, P. and Cala, V. (2011). Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: Environmental implications, J Geochem. Explor., 111, 160-171.

Gonçalves, E.P.R., Boaventura, R.A.R. and Mouvet, C. (1992). Sediments and aquatic mosses as pollution indicators for heavy meatls in the Ave River Basin (Portugal). Sci. Total Environ., 114, 7-24.

Gonçalves, E.P.R., Soares, H.M.V.M., Boaventura, R.A.R., Machado, A.A.S.C. and Esteves Da Silva, J.C.G. (1994). Seasonal variations of heavy metals in sediments and aquatic mosses from the Cavado river basin (Portugal). Sci. Total Environ., 142, 143-156.

Horton, J. and Newson, D. (1953). A Rapid Gas Evolution for Calcium Carbonate Equivalent in Liming Materials. Soil Sci. Soc. Am. Proc. 17, pp. 414-415.

Jung M.C., Thornton I. and Chon H.T. (2002). Arsenic, Sb and Bi contamination of soils, plants, waters and sediments in the vicinity of the Dalsung Cu-W mine in Korea. Sci. Total Environ., 295, 81–89.

Kabata-Pendias, A. and Pendias, H. (2001). Trace Elements in Soils and Plants. CRC Press, London.

Liu, W.X., Coveney, R.M. and Chen, J.L. (2003). Environmental quality assessment on a river system polluted by mining activities. Appl. Geochem., 18, 749–764.

Morgan, J.J. and Stumm, W. (1995). Chemical processes in the environment, relevance of chemical speciation. In “Metals and Their Compounds in the Environment” (E. Merian, ed.). pp. 67-103. VCH, Weinheim.

Nelson, D.W. and Sommers, L.E. (1982). Total carbon, organic carbon and organic matter. In Page, L. (Ed.), Methods of Soil Analysis. Part 2.

Agronomy 9. American Society of Agronomy, Madison, WI, pp. 279-539.

Ritchie, G.S.P. and Sposito, G. (2002). Speciation in soils. In "Chemical Speciation in the Environment" (Ure A., Davidson C.M., eds.), pp. 237-264. Blackwell, Oxford.

Sanchez, J., Vaquero, C. and Legorburu, I. (1994). Metal pollution from old lead-zinc mine works : biota and sediment from oirtzun valle, Environ. Technol., 15, 1069-1076.

Shepard, F.P., and Moore, D.G. (1954). Sedimentary environments differentiated by coarse fraction studies: Bull. Am. Assoc. Petrol. Geologists., 38, 1792-1802.

Tahiri, M., Benyaïch, F., Bounakhla, M., Bilal, E., Gruffat, J.J. and Moutte, J. (2005). Multivariate analysis of heavy metal contents in soils, sediments and water in the region of Meknes (central Morocco). Environ. Monit. Assess., 102, 405–417.

Wang, G.P., Liu, J.S. and Tang, J. (2004). The long-term nutrient accumulation with respect to anthropogenic impacts in the sediments from two freshwater marshes (Xianghai Wetlands, Northeast China). Water Res., 38(20), 4462- 4474.