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Assessment of Heavy Metals Contamination in Spoil Heaps of Ain Aouda Mine (Taza, Morocco)

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ABSTRACT

The purpose of this study is to evaluate the level of heavy metal contamination in the spoil heaps of the former Ain Aouda mine (Taza). In this regard, solid samples of the study area were sampled. The set of analyses carried out have detected the presence of zinc (Zn), lead (Pb), copper (Cu), arsenic (As) and nickel (Ni) that remain in these metal discharges. The calculation of contamination/pollution indices: the Geo Accumulation Index (Igeo), the Enrichment Factor (EF) and the Pollution Index (IP) were used to predict the extent of heavy metal contamination. The results of this study suggest that the spoil heaps reveal polymetallic contaminations allowing the trace metal elements to be classified in the following order Zn > Pb > As > Cu > Ni. Knowing well that the alteration and erosion of this stock of mine waste could contribute to the degradation of the natural environment by these elements that are present.

Keywords: heavy metals, pollution index, Ain Aouda mine, geoaccumulation index, enrichment factor.

INTRODUCTION

Mining is one of the most important sources of heavy metals in the environment. Mining and grinding operations, concentration of ores and disposal of tailings are major sources of environmental contamination (Adriano, 1986). Mining sites are often contaminated by metallic elements; these contaminants affect the natural environment and may harm the environment, thus the concentration of the majority of contaminants sometimes rises to the levels that are toxic for the ecosystem. There are 80 trace elements which are chemical elements constituting the continental crust. Their concentration is very low, less than 0.1%, and they represent only 0.6% of the composition of the Earth's crust (Baize, 1997). Trace metals are metals and metalloids that are considered toxic and the average content of which in soils and sediments is less than 1 g/kg (Gouzy, 2008).

Awareness of the harmful effects of mining discharges on the environment only began in earnest in the 1990s (Ahmedat et al. 2018), while the problem of former mines that have been exploited and abandoned without rehabilitation remains on the agenda (Poulard et al. 2017).

Accumulation of heavy metals in soils is a concern in agricultural production due to their adverse effects on crop growth, food quality and environmental health (Costa and Duta, 2001). Heavy metals are persistent in nature, toxic,have a very high tendency to accumulate in living organisms and adsorb to sediment particles (Wang et al. 2012). Some metals are purely toxic to living things due to their bioaccumulation capacity and persistence in the environment, especially in hydrosystem sediments, given their low biodegradation (Larrose et al., 2010; Diop, 2014; Saher and Siddiqui, 2016). In the design of the assessment of the level of contamination of soils and spoil heaps, it was advocated to be based on the calculation of the geo accumulation index (Müller 1969, Rubio and al. 2000), the enrichment factor and the metal pollution index (Meybeck et al. 1997), after quantifying the concentrations of trace metal elements (Cd, Cr, Cu, Ni, Pb, Zn) in the sampled samples.

MATERIALS AND METHODS

Study area

The Ain Aouda mine is located in the Tazekka massif, which is situated in the province of Taza (Fez-Meknes region). Bounded by the Rif in the north, the Middle Atlas in the south, the Rharb plain in the west and the plain of Guercif in the east, it is the northern termination of the Middle Atlas. Ain Aouda is located 27 km south of the city of Taza, along the road linking this city to the village of Meghraoua (Figure 1).

From the climatic point of view of the study site, the average maximum temperature of the warmest month varies between 34.7 °C and 20 °C, whereas the average minimum temperature of the coldest month varies between 3.8 °C and 19 °C. The bioclimatic stages in the massif are subhumid in the low altitude stations and humid in the high altitude stations.

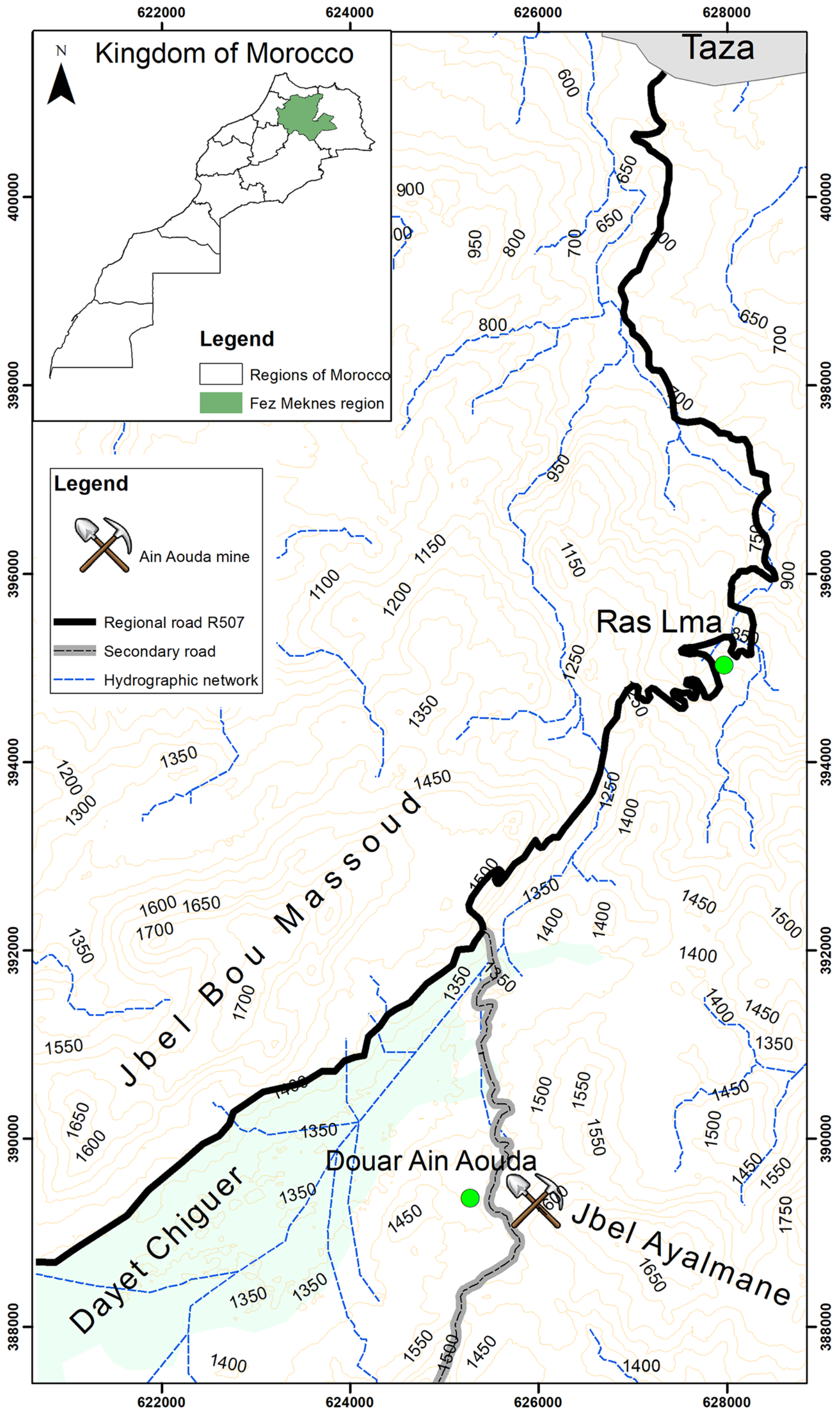

Figure 1. Geographical location map of the Ain Aouda mine

Table 1. Contents of some heavy metals in the continental crust Wedephol (1995)

Heavy metals	Ni	Cu	Zn	Cd	Pb	Fe
UCC (µg/g)	18	14	52	0.1	17	30890

Sampling and samples preparation

Different samples were collected taking into account the physical nature of the sample, exact GPS position of the sample, depth of the sampling point and the identification of the functional unit to which the sample was attached (Lakrim, 2015). The samples were collected with a shovel, stored in new plastic bags, and then transported to the laboratory.

The samples were dried, in the open air, at an ambient temperature of the laboratory, followed by oven drying at 105 °C for 24 hours (Lozet et al. 2002), in order to remove all water. Then, they were ground with an agate mortar and a planetary ball mill, and sieved with a 2 mm stainless steel sieve (AFNOR NF X31-107). The sieved material was finely crushed to obtain a powder of granulometry lower than 250 µm, in order to guarantee the homogeneity and the representativeness of the sample as well as to pass the triacid attack, each sampling of the soil underwent a quartering to have a representative sample.

In order to allow the determination of metallic elements (Zn, Pb, Cu, Cd, As and Ni) by ICP, the samples were placed in solution by triacid etching (HF, $HClO_4$, HNO_3); they were mineralized in hot Teflon beakers. The fractions of the metallic elements contained in the extracted solutions were then read by ICP-AES (Ultima 2) at the Centre National de la Recherche Scientifique et Technique (Rabat, Morocco).

Estimation of pollution intensity

The enrichment factor, geo-accumulation index and pollution index of the collected samples were calculated to assess the intensity of contamination, by comparing measured values against reference values such as averages of elemental contents in the Earth's crust. These parameters are the indicators of pollution level in the environment.

The geo-accumulation index (I geo)

The geo-accumulation index was evaluated on the basis of the values proposed by Müller (1969). This index of empirical character compares a given concentration versus a value considered as geochemical background (Oumar et al. 2014). The following equation (1) designates the calculation of the geo-accumulation index:

$$\text{Igeo} = \log 2 \left(\frac{\text{Cm}}{1{,}5\ \text{Bi}}\right) \quad (1)$$

where: Cm – the concentration of each metal in the soil sample;
Bi – the concentration of the same metal in the background.
Indeed, the coefficient 1.5 is a correction factor that accounts for lithological variations in background levels.

Table 2. Geoaccumulation index scale (Müller, 1981)

Igeo values	Pollution degree
Igeo < 0	Background
0 ≤ Igeo < 1	Not polluted to slightly polluted
1 ≤ Igeo < 2	Moderately polluted
3 ≤ Igeo < 4	Moderately to heavily polluted
4 ≤ Igeo < 5	Heavily polluted
5 ≤ Igeo	Extremely polluted

The normalization element chosen for this study is iron. The trace metal concentrations in the continental crust of Wedepohl (1995) (Table 1) were chosen as the geochemical background. Müller (1981) defined a scale with six classes of geoaccumulation index (Table 2).

The enrichment factor (EF)

The enrichment factor provides the number of times that an element is enriched in relation to the abundance of this element in the reference material. It designates an increase in total content, following anthropic contributions, without prejudging a negative evolution of the quality of the environment (Chassin, 1996).

The standardization element chosen for this study is iron. Trace metal concentrations in NACS (North American Composite Shale, (Mclennan, 2001) were chosen as the geochemical background. The enrichment factor (EF) was calculated according to the following formula in the equation (2).

Table 3. Scale of pollution intensity based on enrichment factor (EF) (Sutherland 2000)

Class	Value	Pollution intensity
1	FE ≤ 2	No or low enrichment
2	2 < FE < 5	Moderate enrichment
3	5 < FE < 20	Significant enrichment
4	20 < FE < 40	Very high enrichment
5	FE > 40	Extreme enrichment

$$\text{EF} = \frac{\text{M (sample)}}{\text{Fe (sample)}} \times \frac{\text{Fe (NACS)}}{\text{M (NACS)}} \quad (2)$$

where: M (sample) – concentration of element M in the sample;
Fe (sample) – concentration of iron in the sample;
M (NACS) – concentration of element M in the geochemical background;
Fe (NACS) – concentration of iron in the geochemical background.

Iron (Fe) was chosen as the normalizing element, because it is associated with fine solid surfaces, its geochemistry is similar to that of many trace metals; and its concentration in natural sediment tends to be uniform (Daskalakis and O'Connor, 1995).

According to Sutherland (2000), enrichment factors are classified into 5 levels of contamination (Table 3).

Metal pollution index (PI)

Heavy metal contamination at mine sites is associated with a mixture of contaminants, rather than a single metal. The calculated metal pollution index is used to assess the overall toxicity of a contaminated soil. According to Chon et al. (1998), it is calculated from the average of the ratios of metal concentrations in soil samples to guideline limit values. These limit values correspond to the assumed tolerable levels in soil suggested by Kloke (1979). The pollution index is calculated by the following equation (3):

$$\text{PI} = \frac{\left(\frac{\text{Cd}}{3} + \frac{\text{Cu}}{100} + \frac{\text{Pb}}{100} + \frac{\text{Zn}}{300}\right)}{4} \quad (3)$$

A pollution index (PI) higher than 1 corresponds to a polluted soil.

RESULTS AND DISCUSSIONS

The geochemical analyses of the spoil heaps of the old Ain Aouda mine revealed excessively high average heavy metal contents (Pb, Zn, Cu, As) (Table 4), which were compared with the normal average contents in the Earth's crust. The average concentrations of Zn, Pb, Cu, and As are of the order of 5799.99, 504.75, 125.62, and 130.77 (mg/kg), respectively. A notable enrichment compared to the average levels chosen as reference was noticed. The concentrations of the studied metals follow the following order: Zn > Pb > As > Cu.

These high average contents are the result of the storage of mining heaps coming from the exploitation of calamine, cerussite, galena and other minerals in the Ain Aouda mine.

Table 5 shows the geo-accumulation index values for the different sampling stations and for each metal. The geo-accumulation indices for nickel are all below 0. This indicates that the stations are not polluted by this metal.

According to Müller's (1969) classification, the Igeo classes of lead (Pb) were 'Moderately contaminated', 'Moderately contaminated to severely contaminated', 'Severely contaminated', 'Severely to extremely contaminated' and 'Extremely contaminated' for stations (S6, S7, S9), (S2), (S5), (S8) and (S1, S3, S4) respectively. In turn, zinc (Zn) Igeo classes were 'Not contaminated', 'Moderately contaminated', 'Severely to extremely contaminated' and 'Extremely contaminated' for stations (S1, S7), (S6, S9), (S2), (S3, S4) and (S5, S8) respectively, while arsenic is absent in stations (S6, S7 and S9), but it showed Igeo indices that are respectively 'Not contaminated to Moderately contaminated', 'Moderately

Table 4. Average contents of the trace elements of the spoil heaps of Ain Aouda compared to the Clarke and AFNOR

Heavy metal	Zn	Pb	Cu	As	Ni
Average contents in the waste rock piles (g/t)	5799.99	504.75	125.62	130.77	2.87
Average contents in the earth's crust (g/t)	101	16	62.50	5	75
AFNOR	300	100	100	30	50

Table 5. Results of the geo-accumulation index

Station	I geo Zn	I geo Pb	I geo Cu	I geo Ni	I geo As
S1	-6.01	5.65	2.29	-5.04	1.78
S2	3.85	2.56	2.22	-5.46	1.09
S3	4.71	5.15	3.13	-5.04	2.17
S4	4.70	5.37	0.33	-7.04	2.17
S5	7.54	3.92	1.92	-6.04	1.51
S6	1.36	1.28	-2.23	-3.04	-2.79
S7	-0.18	1.21	-2.42	-2.87	-3.21
S8	7.38	4.42	2.29	-7.04	0.06
S9	1.47	1.35	0.53	-7.04	-3.21

contaminated', 'Moderately contaminated to severely contaminated', for stations (S8), (S1, S2 and S5) and (S3, S4). In turn, copper manifested the following geo-accumulation index classes according to Müller, 'Not contaminated to Moderately contaminated' in stations (S4) and (S9), 'Moderately contaminated' for station (S5), 'Moderately contaminated to severely contaminated' for (S1) and (S2) and 'Severely contaminated' for station (S3).

Regarding the results of the enrichment factor (Table 6), it appears that the lowest values of EF in nickel (EF < 2) are obtained in all sites except station (S9) which proves a moderate enrichment (2 < FE < 5).

Stations (S1), (S2), (S3), (S4), (S5), (S8) and (S9) reveal surprising values of zinc enrichment factor which reach 3996.30 in station (S8), it is an extreme enrichment (EF > 40). In turn, the enrichment of stations (S6) and (S7) is respectively 'very strong' and 'significant'.

Stations (S1), (S3), (S4), (S5), (S8) and (S9) also show extreme lead enrichment (EF > 40), with values fluctuating between 114.85 and 1351.80. In turn, stations (S2) and (S6) prove a very strong enrichment given their values between 5 and 20, while station S7 showed a significant enrichment in lead (20 < EF < 40).

Copper enrichment is extreme in stations (S5) (S8) and (S9), very high in station (S3), significant in stations (S1) and (S2), moderate in station (S4) and (S6) and non-existent or low in station (S7).

Stations (S1), (S2), (S3), (S4) and (S5) show extreme arsenic enrichment, as the values of this enrichment fluctuate between 59.43 and 97.26. In turn, the arsenic enrichment in station (S8) is very high because it is between 20 and 40. However, stations (S6), (S7) and (S9) reveal a significant enrichment as their values are between 6.67 and 16.41.

It is easy to notice that zinc, lead and arsenic are the elements that stand out the most with an extreme enrichment in several stations, while copper has an extreme enrichment in 3 stations.

In Table 7, the results obtained indicate IP values that vary between 0.25 in station (S7) and 17.96 in station (S5).

With the exception of Stations (S6), (S7) and (S9) which have a PI lower than 1, all stations show polymetallic contamination. Except that the

Table 6. Results of enrichment factor

Station	FE Zn	FE Pb	FE Cu	FE Ni	FE As
S1	208,62	163,27	15,918	0,14	97.26
S2	46,82	19,15	15,170	0,07	89.09
S3	85,05	114,85	28,402	0,10	78.87
S4	85,43	135,47	4,156	0,02	59.43
S5	2457,96	218,15	49,915	0,20	64.38
S6	31,65	30,23	2,835	1,49	16.41
S7	5,93	15,63	1,351	0,91	6.67
S8	3996,30	514,57	117,308	0,18	35.49
S9	1470,82	1351,80	764,842	4,01	8.95

Table 7. Results of pollution index

Station	PI
S1	9.36
S2	2.10
S3	5.41
S4	5.06
S5	17.96
S6	0.40
S7	0.25
S8	16.61
S9	0.54

extremely high PI recorded for Stations (S1), (S5) and (S8) affirm the extremely harmful character of these abandoned heaps, which constitute a perennial source of heavy metal contamination for the environment.

The study notes that the majority of the samples taken from the spoil heaps are extremely enriched in zinc, lead, arsenic and copper, which reflects the high anthropogenic load of these metals in the area, with the exception of nickel, which has little or no enrichment. This corroborates with the mineralogical nature of the spoil heaps deposited on the bedrock, which constitute an important source of pollution insofar as they generate the effluents that can be loaded with metals, due to their exposure to meteorological agents, provoking a series of reactions that lead to the solubilization of the metals present in these spoil heaps. Although sulfide minerals are naturally present in rocks, mining activities amplify the release and concentration of trace elements in the soil.

The calculation of the enrichment factor (EF) of different metals allows evaluating the intensity of a metallic pollution by distinguishing the anthropic signal from the natural signal. The calculation of this indicator can only be defined in relation to the natural geochemical background, corresponding to pre-anthropic metal contents (Alexander et al. 1993; Sutherland et al. 2000; Mil-Homens et al., 2006). The average enrichment factor values allow the heavy metals to be ranked in the order of Zn > Pb > As > Cu > Ni. Similarly, the order of magnitude for heavy metals based on average geo-accumulation index values is: Zn > Pb > As > Cu > Ni. These contaminants are not easily eliminated by living organisms, and this is because they are not essential to life. Thus, they can enter the processes of bioaccumulation and bioconcentration.

Zinc and lead are the most enriched and important, for the reason that the old Ain Aouda mine is a mine that was used to extract 8 species of calamine, smithsonite, hemimorphite and hydrozincite. Zinc hydroxides are also present, they are the result of the karstification that affected the sulfide mineralization in the Ain Aouda mine. The existence of cerusite and galena was also noted. The afore-mentioned minerals are strongly present in the heaps, they contaminate the soils on which they are deposited, but also those of the surroundings; thus, these grounds become unfit for the growth of vegetation, but also unfit for the development of human activities.

In addition, arsenic is enriched and accumulates in the mine waste rock where it can contaminate the surrounding soils. It is mainly associated with pyrite but also with other sulfides such as arsenopyrite, marcasite (FeS_2) and galena (PbS). Arsenic can be released during the oxidation process of the sulfide ores (chemical release) or it can be disseminated by the flight of dust from the tailings into the atmosphere. It has harmful effects not only on the quality of soils and surface waters but also on organisms in the lower levels of the food chain where it accumulates and persists.

CONCLUSIONS

The results of this study have allowed highlighting undesirable impacts of mining on the environment. The study area has a high potential for pollution due to mine tailings left untreated, which disturb the aesthetics of the area, and which require rehabilitation.

The concentrations of the five heavy metals show values above the Earth's crust and even above the AFNOR standards. The determination of the metallic contamination with the help of quantification tools, the enrichment factor (EF) and the geo-accumulation index (Igeo), proved that the spoil heaps are polluted by Zn, Pb, As, Cu and Ni, respectively. Knowing that, the calculations of these indices revealed extreme contamination by zinc, lead and arsenic in more than one station. As a conclusion, the polymetallic contamination was confirmed by the calculation of the pollution index, which gave values higher than 1 in six stations.

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