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Assif El Mal River: source of human water consumption and a transfer vector of heavy metals

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ABSTRACT

The mining and metallurgical mines that were abandoned with their residues constitute a source of metal pollution affecting the quality of water resources and soil. It is the case of an abandoned mining site Assif El Mal drained by the Assif El Mal River. In fact, these waters are a source of consumption without any treatment by the local population either directly or through their storage in reservoirs. A spatial variation of physicochemical parameters is determined to follow and monitor the behavior of some metals (Pb, Zn, Cu, and Al), from the abandoned mining district, in water and sediment samples along the river till the reservoirs. Also, an assessment of metal contamination level and toxicity of water is studied using the sequential extraction procedure (BCR). The results showed that the metallic load in water exceeds standards for human consumption, especially in the vicinity of the mine and the storage tanks. These levels range from 0.3–17, 0.02–0.05, 0.3–2.8, 0.03–0.1, 2.6–5.1 mg L1, respectively, for Al, Ni, Fe, Pb, and Zn. The potential toxicity of heavy metals in sediment is due to their mobile fraction exchangeable/acid soluble often high (averaging 41 Pb, 52 Zn, and 68% Fe).

Keywords: Assif El Mal River; Heavy metals; Water quality; Sediment; Sequential extraction

1. Introduction

Mining is one of the most important sources of heavy metals in the environment. Mining and milling operation together with grinding, concentrating ores and disposal of tailings, along with mine and mill wastewater, provides the obvious sources of contamination [1]. Heavy metal contamination has been one of serious problems in the vicinity of abandoned mine sites. These heavy metals have a potential to contaminate soil and water. They can be dispersed and accumulated in plants and animals, and taken in by human beings as consumer. Human health risk assessment has been used to determine if exposure to a chemical, at any dose, could cause an increase in the incidence of adverse effect to human health [2].

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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 wastewater [3]. Many studies have been conducted on heavy metal contamination in soils, plants, waters, and sediments from metalliferous mines throughout the world [4,5]. The extent and degree of heavy metal contamination around the mines vary depending upon geochemical characteristics and mineralization of tailings. For example, tailings containing large quantities of sulfide minerals could influence nearby agricultural lands and streams. Mining activities have a relevant influence on the quantity and quality of water resources in the surrounding environment. The deterioration of water quality is caused by the residues of ore exploitation and processing has been recognized worldwide [6–9]. Therefore, the chemical contamination of water systems at abandoned mining sites demands investigation strategies capable of describing sources and pathways of contaminants and containment strategies devoted to limit the diffusion of toxic components.

In Morocco, various mines were distributed all over the country (Kettara, Goundafa, Kodia Hamra, Karkour, Sidi Bou Othmane, and Assif El Mal) and have been actively exploited, until recent decades most of these mines were closed due to economic reasons. The code Moroccan mining has indeed been prepared at a time when the environmental protection was not a concern priority. Abandoned mining sites pose physical safety and environmental hazards recognized by the United Nations as one of the major outstanding environmental problems related to mining [10]. After mine closing, mine waste materials, including tailings, were left without full environmental treatment. Thus soils, plants, waters, and sediments in the vicinity of the mines have been contaminated by potentially toxic elements from tailings by clastic movement through wind and water. Because these emotions can induce a transport to the watercourse of pollutants attached to particles solid [11]. So, these elements and their compound are often transported long distances by water with or without chemical modifications. The transformation reactions usually lead to compounds more toxic than the original item [12]. There are abiotic and biotic transformation mechanisms involving heavy metals and metalloids, in which they can affect the pathways of reactions in a synergistic fashion. In fact, amongst the biotic transformation, the microbial processes are the metal solubilizations which increase their bioavailability and potential toxicity [13]. For example, the bacteria's carry out chemical transformations of heavy metals by oxidation, reduction, methylation, and demethylation mechanisms, making these metals very toxic. In other way, sorption on mineral surfaces is an important process that can bind and sequester heavy metals and other aqueous contaminant ions. Sorption can dramatically reduce the mobility of contaminants in groundwater and, in the case of redox-sensitive elements, result in their transformation into a less (or more) toxic species through reduction or oxidation reactions.

For all the mines in this region, few studies have been done to evaluate the impact of heavy metals in water resources and surrounding soil of the mine [14].

In this context, we assessed in the present work the soil contamination in the vicinity of the abandoned Assif El Mal mine. The sediment and water of consumption along the river running through the mine, until their storage in reservoirs, was also analyzed in this study. This was done by using the Pollution Index (PI) and through the evaluation of the total metal content of the current status in these solid wastes (tailings) and water, together with sequential speciation to understand the environmental risk potential of these wastes. The purposes of this study were to investigate also, the distribution of metal speciation in sediment and the metal charge of different particle-size fractions of these sediments studied.

2. Materials and methods

2.1. Study area

In rural areas, the majority of the population has neither a supply of clean drinking water or proper sanitation. This is the case of the valley Assif El Mal, a tributary left bank of the Tensift River situated at 80 km southwest from the Marrakech city. It drains a watershed of 517 km^2, where people resort to archaic method as the only source of water for any purpose. The river water and water stored in reservoirs (which are a reservoirs built traditionally buried in the ground fed by streams of water from this river) are the principal water supplies available in the region. This river crosses some metallic deposits along its path and the main mine.

2.2. The abandoned mine

The ***Assif El Mal*** mine is a polymetallic Zn–Pb (Cu, Ag) veins located 100 km southwest of Marrakech on the northern flank of the High Atlas Range [14] (Fig. 1 (a)). Discovered in the 1920s by French prospectors and mined underground between 1948 and 1960, the Assif El Mal deposit was operated by the Assif El Mal Mining Society Ltd., producing ~1 Mt of ore at 8% Zn, 2% Pb, <1% Cu, and 500–2,300 g/t

Ag making it the greatest producer of zinc in Morocco. The major period of zinc mining ended with the closure of the underground mine in 1960 [15].

The deposit is localized in primary schists are penetrated by igneous rocks: dolerite and microgranite. The operated lode consists of sphalerite, galena, chalcopyrite, and pyrite. The oxidation zone is very small and minerals found there are diverse (malachite, azurite, carbon, calchantite, and cerussite). Note that sphalerite dominates in minerals. Galena is composed of dolomite, quartz, calcite, and barite. Dolomite appears to be the dominant ore from the dross zinc [16].

The climate of the studied zone is Mediterranean, in the limit of the semi arid and the arid climate. Climatic conditions in the region are characterized by long periods of heat and drought, usually extending from April to September, interrupted by relatively short rainy periods, with occasional heavy rain events. Average annual precipitation calculated over the last 10 years is equal to 235 mm.

2.3. Sampling collection and analytical methods

2.3.1. Water

Water samples were collected basis from the rivers and the reservoirs as indicated in Fig. 1, in November 2010, represents the dry seasons.

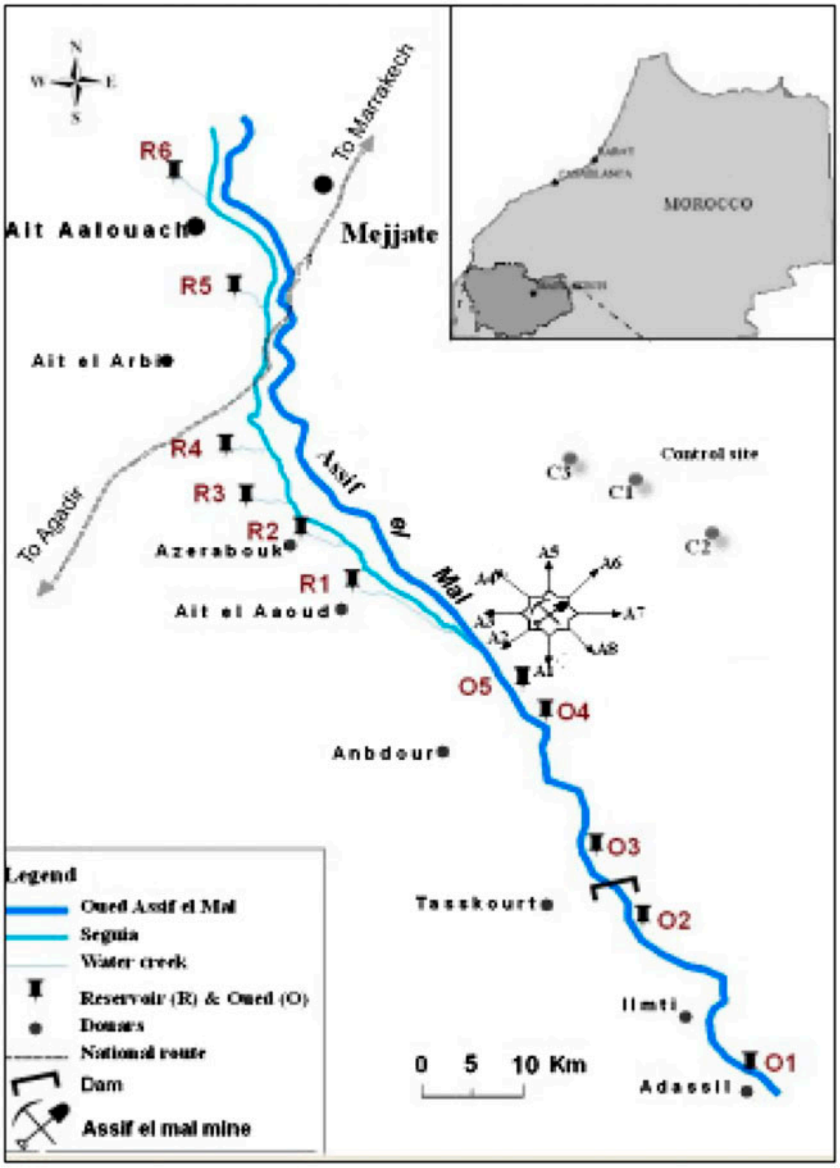

Fig. 1. Map of sediment and water sampling sites in the study area.

The propylene containers were used for sample collection. Before use, the propylene containers (500 ml) were first rinsed with the water samples and there after immersed about 15 cm below the surface. After collection, Temperature, pH, and conductivity were determined in the field using portable measuring (WTW Multiline). The samples for total metal concentrations were acidified in the field with grade HNO_3, while samples for speciation studies were taken to the laboratory and filtered under pressure through acid washed 0.45 mm cellulose nitrate membrane filters.

Water samples were analyzed for a number of dissolved trace metals, major anions (Cl^-, NO_3^-, and SO_4^{2-}) in nonacidified waters were measured by ion chromatography (IC).The trace elements (Fe, Cu, Pb, Zn, and Ni) were determined using inductively coupled plasma–atomic emission spectrometry (ICP-AES).

2.3.2. Sediment

For the objective to monitor the transport of micropollutants related by small metal deposits along the River, we performed five samples at the sites shown in Fig. 1 with two depths in each station (0–10 and 10–20 cm). At each station, three sediment samples were collected and mixed at a time to ensure that the sample was representative for this station.

In order to assess the impact of the Assif El Mal mine residues on the surrounding environment, a total of 88 samples were collected in the vicinity of the mine; according eight axes in different direction (A1–A8: about 11 samples along each axe are homogenized) with a 40 m of perimeter. Each of these sampling lines is oriented towards specific receptor media (Assif El Mal River, village, forest (field of livestock), etc.). In undisturbed core of the mine, a three tailing sample is also collected.

Finally six surface sediment (<5 cm depth, Oxic area) samples were taken using a grab sampler, we assessed the degree of metal transfer to the storage reservoir water supply.

Samples were kept in air sealed plastic bags and placed in a portable cooler at 4˚C, transported to the laboratory and stored in the freezer at −20˚C until further analysis. The sediment samples were oven-dried at 60˚C for 24 h and the coarser material (>2,000 μm) was removed by sieving.

2.4. Total metal concentrations

Soil edaphological parameters (pH, organic matter (% O.M.), electrical conductivity (EC), and carbonate content (% CO_3) were measured following the procedure procedures described in the Official Methods of Soil Analysis envisaged by Aubert [17].

Total heavy metal concentration was determined by ICP AES after digestion of the samples. 0, 50 g dry sample was weighted in a Teflon beaker and 7 mL HNO_3 (65% w/w), 2 mL HF (40% w/w), and 1 mL $HClO_4$ (60% w/w) were added. The Teflon beaker was placed on a hotplate until total digestion. After digestion, the sample solution was allowed to air-cool and then diluted with deionized water to 50 ml.

2.5. Speciation of heavy metal by BCR sequential extraction

Although the separation of various chemical forms of heavy metals is very difficult, the use of sequential extraction methods in this way provides an important approach. The sequential extraction was performed using the tree-step procedure recommended by BCR, it was applied to assess heavy metal fractionation in the samples (<100 μm fraction). This method was described in detail by Sabra et al. [18]. The solid residue left at the end of these extraction steps represents the residual fraction. It comprises heavy metals which are strongly bound to the crystalline lattice of the sediments and which cannot be released by any of the reagents used in the previous steps. The sediments must be continually in suspension during the extraction. The extracts are filtered through a 0.45 μm membrane prior to ICPAES determination. The method details are presented in Table 1.

2.6. Internal check recovery

Results obtained by sequential extraction are particularly susceptible to irreproducibility, since errors can easily be propagated between steps; a validation of the analytical results was done by recovery experiments. So, the recovery of the sequential extraction method was calculated as follows: Recovery = [C Fraction 1 + C Fraction 2 + C Fraction 3 + C Residue/C total digestion] × 100.

2.7. Particle size analysis

The hydrogen peroxide method of Robinson [19] is now universally used for particle sizes identification. On trying to adopt this method, a sample is pipetted at different times and depths of the suspension of the sample in a graduated cylinder (1 L). Five size classes were separated: clay (0–2 microns), fine silt (2–20 microns), coarse silt (20–50 microns), fine sand (50–200 microns), and sand coarse (200–2,000 microns).

Table 1
Modified BCR four-step sequential extraction procedure

Step	Fraction	Extraction reagent and method	Extracted components
A	Exchangeable, water, and acid soluble	Acetic acid CH_3COOH (0.11 mol/l), pH 2.85, 16 h	0.11 mol/l acetic acid
B	Reducible	Hydroxyl ammonium chloride NH_2OH_HCl (0,1 mol /l), pH 2	Iron–manganese oxides
C	Oxidizable	Hydrogen peroxide 30% H_2O_2 (8.8 mol /l), 2 h at 85°C, followed by CH_3COONH_4 (1 mol /l), pH2, 16 h	Sulphides/organics
D	Residual	Mix acid HNO_3 (7 ml) + $HClO_2$ (1 ml) + HF (2 ml)	Metals bound in lithogenic minerals

2.8. *X-ray diffraction*

The determination of mineral phases was carried out applying the X-ray diffraction method on the initial sediment sample as well as on soil and the tailing of mine. Operational parameters: Cu tube, Kα 1.540 Å radiation, graphite crystal monocromator, and sparkler detector; the instrumental conditions used are: voltage 40 kV; current 30 mA; and slit 1, 1, 1, and 0.5 mm.

2.9. *Pollution Index*

Integrated PI was used in this study to evaluate the degree of trace metal contamination [20–25]. Soil PIs and water pollution index (PIw), which are calculated computed by averaging the ratios of the element concentration to the hazard criteria, the permissible level for each element (as shown in the Eqs. below (1) and (2)).

A PI of >1.0 was only found in the tailings, which are considered to be multielement contaminated and recommended for treatment. With the exception of the tailings, however, the PI in most soils sampled was <1.0. Also, if any index over 1.0 indicates that, on average, metal concentrations are above the permissible level [26,27] and any element enrichment may be from anthropogenic inputs or natural geological sources [21]. It is generally agreed that most heavy metal contamination in the surface environment is associated with a cocktail of contaminants rather than one metal. Thus, many workers have used a PI of soils to identify a multielement contamination resulting in increased overall metal toxicity. Although equations for the calculation of the PI differ for individual researchers, the basic concept of the method is almost the same. In general, the PI can be computed by averaging the ratios of metal concentrations in sampled soils to the "assumed permissible level" of metals. Whose, the tolerable level is the element concentration in the water considered safe for human consumption [23–28]. Also, the tolerable levels for soils suggested by Kloke [28] were adopted for the assumed permissible levels.

$$\mathrm{PIs} = \frac{\sum \frac{\text{Heavy metal concentration in soil}}{\text{Tolerable level}}}{\text{Number of heavy}} \tag{1}$$

$$\mathrm{PIw} = \frac{\sum \frac{\text{Heavy metal concentration in soil}}{\text{Tolerable level}}}{\text{Number of heavy}} \tag{2}$$

3. Results and discussion

3.1. *Physicochemical properties of the river sediment, reservoir sediment, tailing, and soil of the mine*

Heavy metal pollution of the surface environment due to mining carried out in past is commonly associated with many contaminants, rather than with a single element. One approach for comparing the metal concentrations is to compute an index which averages the accumulation of each metal in a sample. As expected, the highest PIs values occurred in the tailings and also in the reservoirs sediment, indicating that these residual deposits are the main source of chemical contaminants.

The PIs calculated for representative samples in the studied area, it was 13.09 for the tailing samples, varied from 1.73–3.85 in the mining soils around the mine and 1.91–3.5 was recorded in the reservoirs sediment, with a lowest values (0.1–0.3) in the river sediments. This, showed that the tailings contains the high level of metal likely to be toxic to the ecosystem as defined by Nimick and Moore [21] and Ferreira Da Silva et al. [29]. The tailings have presented a fine unconsolidated texture that accelerated the dispersion of the particles rich in heavy metals. Exposure of tailings to air, oxidation, and climatic conditions favored the release of heavy metals [30] which are often a threat to the environment [31–33]. Then they can more contaminate ecosystem, consequently, which constitute a great risk to the population.

Among the calculated results, PIs values was more than 1 indicating that the sediments was contaminated by heavy metals, which could be a problem for human and aquatic life. Indeed, some studies had specified that Zn speciation; especially soluble phases had an important influence on lung [34]. On the other hand, Pb is considered as a serious public health problem particularly for children. The adverse toxic effects caused by Pb on human health were well documented [35]. Neurological defects, renal tubular dysfunction, and anemia are the most characteristics of Pb poisoning [36].

Chemical analysis of mine soil revealed high concentrations of Cu, Zn, Pb, Fe, and Ni (Table 1). The values ranging 53 ± 8.5–117 ± 15 mg/kg Cu, 533 ± 23–2042 ± 36 mg/kg Zn, 74.1 ± 6.4–165.8 ± 9.8 mg/kg Pb, 2,210 ± 65–4,060 ± 58 mg/kg Fe, and 4.8 ± 1.2–15.5 ± 1.8 mg/kg Ni were recorded for the residues around the mine, with a maximum values in the first four axis (A1–A4) in direction of the river (Fig. 1). The very high values were marked in the tailing (226 ± 17; 4,112 ± 73; 511.9 ± 35.6; 1870 ± 45; and 17.8 ± 2.4 mg/kg, respectively for Cu, Zn, Pb, Fe, and Ni). In the same direction of contamination, the interesting values were registered in the sediment of reservoirs that ranging between 7 ± 0.5–10 ± 2; 2018 ± 56–3,796 ± 108; 39.1 ± 4.3–50 ± 7; 1,019 ± 32–9,901 ± 93; and 12.2 ± 1.4–23.3 ± 4.1 mg/kg of Cu, Zn, Pb, Fe, and Ni respectively.

However, in the upstream of the mine, represented by the river sediments stations, we observed lowest values of all elements in the two studied depths (particularly, in the second depth, 10–20 cm). Excepted the last station nearing to the mine (O$_5$) where the high levels in terms of analyzed elements

Table 2
Geochemical characteristics, PIs and total concentrations of some heavy metal (Cu, Zn, Fe, Ni, and Pb) of the samples in the study area (Soil and tailing samples surrounding Assif El Mal abandoned mine, river s sediment (O$_a$: 0–10 cm; O$_b$: 10–20 cm), and sediment of water reservoirs)

	pH	EC (μS/cm)	$CaCO_3$ (%)	OM (%)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	PIs
O1$_a$	8.09	215	1.8	1	3.61	44.58	14.1	3,200	1.28	0.09
O1$_b$	7.98	257	1.5	1	2.52	55.04	9.8	2,600	1.56	0.08
O2$_a$	8.06	227	1.3	0.1	1.46	48.68	16.3	3,930	3.1	0.10
O2$_b$	8.05	226	1.9	0.1	0.94	70.46	14.2	3,240	1.87	0.11
O3$_a$	8.15	231	3.1	1.5	8.12	97.9	16.7	2,460	2.24	0.15
O3$_b$	8.15	243	3.2	1	7.44	64.2	13.8	3,780	1.95	0.12
O4$_a$	8.18	255	2	1.7	19.7	88.74	16.2	3,850	4.25	0.18
O4$_b$	8.22	228	2.7	1.3	10.7	43.76	12.4	2,120	3.3	0.11
O5$_a$	8.19	230	3.6	1.9	25.56	110.6	53	4,208	5.69	0.32
O5$_b$	8.31	212	3.4	1.7	22.94	100.8	38.9	3,790	4.43	0.26
A1	7.94	390	2.8	2.23	94.2	932	118.4	2,380	11.4	1.73
A2	8.42	210	2.45	0.56	102.3	816	122	2,600	14.8	2.41
A3	8.05	200	2.1	2.5	104	1,460	165.8	3,100	13.2	3.08
A4	7.83	592	1.75	0.84	117	2,042	134.2	3,900	15.5	3.85
A5	7.48	590	2.1	2.96	68.1	533	86 .5	2,210	7.3	1.62
A6	7.8	417	2.8	2.19	74	739	74.1	3,360	6.3	1.68
A7	8.32	710	2.45	5.06	53.9	762	83.3	3,200	7.6	1.68
A8	8.12	618	2.76	2.52	62.8	911	77.6	4,060	4.8	1.70
Tailing	3.24	2,140	1.75	0.72	226	4,112	511 .9	1,870	17.8	13.09
R1	7.52	164	5.2	9.36	7.0	2,018	42.4	1,134	19.4	1.91
R2	8.11	187	5.1	11.7	6.69	2,761	39.1	1,065	22	2.53
R3	7.96	242	7.0	12. 3	8.21	3,377	51.0	1,019	21.7	3.07
R4	7.82	260	9.3	15.6	9.28	3,796	48.4	7,074	20.4	3.41
R5	7.74	370	21.1	11.7	9.99	2,280	50.6	9,901	23.3	2.17
R6	8.18	1,485	14.2	13.9	9.68	3,564	46.5	7,338	12.2	3.50
Reference	8.29	120	2.89	2.54	Nd*	31.4	Nd	932.8	Nd	0.03
Guideline values					100	300	100		50	

*ND, not detected (lower instrumental detection limit).

Table 3
Pearson correlation coefficients between total metals and soil chemical properties

	Correlation coefficient, *r*			
	pH	EC	$CaCO_3$	OM
Cu	-0.70^{**}	0.63^{**}	−0.29	−0.28
Zn	-0.49^{**}	0.55^{**}	0.53^{**}	0.70
Pb	-0.89^{**}	0.76^{**}	−0.14	−0.13
Fe	0.15	0.12	0.76^{**}	0.63
Ni	−0.30	0.20	0.56^{**}	0.66

**Significant at $p < 0.01$; *significant at $p < 0.05$.

were accumulated (Table 1), allowing to confirm that the origin of reservoir sediment contamination are the mining residues.

Others like the pH, carbonate, and organic matter contents are the principal soil characteristics that determine the capacity to retain heavy metal pollutants. The obtained results for all soil samples are summarized in Table 1. Thus, all samples have presented a pH levels between 7.5 ± 0.23 and 8.5 ± 0.12 which are similar to the reference samples, excepted, the tailing samples that mentioning a very acidic pH 3.24 ± 0.11.

This low pH levels of the tailings may be due to the weathering of sulfide minerals. The carbonate contents of river sediment (1.3 ± 0.4–3.6 ± 0.3%) and the mine soils (1.75 ± 011–3.4 ± 0.15%) have the lowest average, while the highest contents were reported in the reservoir sediments and reached 21 ± 0.5%. This ascertainment indicates a calcareous nature of these samples (Table 1).

Generally, the range of organic matter is between 0.5 ± 0.1 and 3 ± 0.5% (Table 2). These values are similar to that found for the control samples. In some points, around the mine, the percentage reached 5 ± 1% and could due to some localized agricultural activities and a high content of organic matter (15 ± 1%) accumulated in the reservoirs sediment due to local contamination (population activity).

Correlation studies of total heavy metal concentration and soil chemical properties were presented in Table 3. The results typically show statistically significant correlation. Negative and significant correlations ($p < 0.01$) were obtained for pH and Cu, Zn, and Pb, while a very poor correlations were noted for Fe and Ni. As pH increases, the negative charge on such surfaces is increased. These negatively charged sites may increase the probability of absorption of positively charged ions in the surrounding soil by increasing cation exchange capacity (CEC). CEC increases with increasing pH and so does the capacity to absorb cations. The effect of electrical conductivity (EC) is strongly pronounced on availability concentration of Zn, Pb, and Cu in soil, therefore, a positive and significant correlations ($p < 0.01$) were also obtained in one hand, for EC and Cu, Zn, and Pb. The solubility of these elements in surrounding soil was mainly increased by conductivity of soil. Soil EC can serve as a proxy for soil physical properties such as organic matter [37] and cation exchange capacity [38]. High concentration of Ca may also lead to the reduction in Fe solubility.

In the other hand, we observed a positive correlation between the carbonate (significant at $p < 0.01$) and the organic matter (no significant at $p < 0.05$) and Zn, Fe, and Ni. Finally, the statistical analysis showed significant correlation ($p < 0.05$) between the three pollutants Cu, Pb, and Zinc along the axes A1, A2, A3, and A4, situated in the west of the mining site (direction to the Assif El Mal river).

3.2. Partitioning of metals in soil and sediment

It is evident that only a part of the total amount of heavy metals in soils may be regarded as bioavailable and potentially toxic in the environment. Hence, the total concentration is not sufficient for the estimation of the of heavy metal pollution extent [39]. Recover percentage fractionations of heavy metals for all soil samples and the fractionation pattern are mentioned in Table 4 and Fig. 2, respectively.

For all the heavy metals, except in very few cases, the fractional total did not differ much from the total metal concentration, indicating that enhanced recovery was achieved from the procedure used. The ranges of metals in each of the four fractions are shown in Table 4.

The F1 concentrations for mine soils samples of the axis (A1, A2, A3, and A4) taken from the river area direction ranged from 15.45 ± 2.15 to 35 ± 5% of the total metal of Zn and from 14.4 ± 0.8 to 21.67 ± 0.23% of the total metal of Pb, with a high values observed in tailing samples (an average about 41 ± 2 and 35 ± 4% for Zn and Pb, respectively). The other samples (axis A5–A8, and the river sediment) located at distances further away from the mining residues present the following results: The F1 concentrations ranged from 2.75 ± 0.25 to 14.90 ± 1.3% for Zn and from 6.18 ± 0.36 to 10.19 ± 1.21% for Pb. For this fraction (F1), Zn concentrations were significantly higher than Pb in the majority of the soil samples. The important values for Zn were recorded in reservoirs sediment (ranged between 8 and 19%, and 9.11 ± 0.73 to 17.44 ± 2.12% for Pb).

Concerning the reducible form fraction F2 of Zn and Pb that mentored an average low, especially in the river and the reservoirs sediment, the reason is that the mine soil registered 19 ± 2% of Zn and 25 ± 4%

Table 4
The efficiency of metal recovery attained by BCR sequential extraction used

	Zn			Pb			Cu		
	$\sum$4 fractions (mg/kg)	Total (mg/kg)	Recover (%)	$\sum$4 fractions (mg/kg)	Total (mg/kg)	Recover (%)	$\sum$4 fractions (mg/kg)	Total (mg/kg)	Recover (%)
O 1$_1$	46.1	44.58	103.4	15	14.1	106.4	3.87	3.61	107.2
O1$_2$	51.62	55.04	93.8	10.4	9.8	106.1	2.7	2.52	107.1
O2$_1$	44.74	48.68	91.9	15.8	16.3	96.9	1.56	1.46	106.8
O2$_2$	72.12	70.46	102.4	13.8	14.2	97.2	1.01	0.94	107.4
O3$_1$	100.14	97.9	102.3	15.9	16.7	95.2	7.92	8.12	97.5
O3$_2$	61.86	64.2	96.4	12.8	13.8	92.8	8	7.44	107.5
O4$_1$	90.07	88.74	101.5	17.3	16.2	106.8	21.2	19.7	107.6
O4$_2$	39.86	43.76	91.1	13.1	12.4	105.6	11.4	10.7	106.5
O5$_1$	118	110.6	106.7	56.5	53	106.6	27.2	25.56	106.4
O5$_2$	96.85	100.8	96.1	41.2	38.9	105.9	24.5	22.94	106.8
A1	896	932	96.1	109.8	118.4	92.7	101	94.2	107.2
A2	851	816	104.3	118	122	96.7	110	102.3	107.5
A3	1,550	1,460	106.2	158.6	165.8	95.7	109	104	104.8
A4	1,908	2,042	93.4	127.9	134.2	95.3	125	117	106.8
A5	562	533	105.4	91.4	86.5	105.7	73.1	68.1	107.3
A6	708	739	95.8	78.6	74.1	106.1	79.3	74	107.2
A7	726	762	95.3	88.1	83.3	105.8	58	53.9	107.6
A8	885	911	97.1	82.2	77.6	105.9	67.3	62.8	107.2
Tailing	3,890	4,112	94.60	492	511 .9	96.11	212	226	93.81
R1	3,786	4,112	92.1	488.6	511.9	95.4	209.4	226	92.7
R2	1,870	2,018	92.7	45	42.4	106.1	8.1	7	115.7
R3	2,542	2,761	92.1	41.4	39.1	105.9	7.44	6.69	111.2
R4	3,548	3,377	105.1	48.1	51	94.3	9.1	8.21	110.8
R5	4,028	3,796	106.1	51.3	48.4	106.0	10.2	9.28	109.9
R6	2,098	2,280	92.0	54.1	50.6	106.9	11.3	9.99	113.1

of Pb. The fractions F1 (exchangeable) and F2 (related to carbonates) provide information on the bioaccessibility of metals in the most mobile fractions [3,40], which increase the toxicity risk in our studied area. In the majority of samples, the important amounts of Zn and Pb were associated with the oxidizable fraction (F3), it was mainly for the mine soil and sediment of reservoirs, that represent respectively, a average percentages of the total metal content between 10–39.05 ± 2.15%, and 13.23 ± 1.56–38.15 ± 3.45% for Zn and 22 ± 3–32 ± 1%, and 14 ± 0.5–30 ± 4% for Pb. It is noted that the copper content of F1 and F2 fraction was low in all samples; especially acid soluble/exchangeable fraction (F1) that was low to 10%, showing less direct toxicity to environment. 15 ± 2–35 ± 4% and 50 ± 7–83 ± 5% of total Cu was recorded respectively in oxidizable fraction (F3) and residual fraction (F4) for all samples, this highest observed percentage of the residual species for Cu concurred with the results from other studies [41–43].

3.3. Distribution of heavy metals in the different granulometric fractions

According to Table 5, heavy metals were generally more concentrated in the fine granulometric fractions than in the coarse ones, while this trend was not observed for the tailing samples.

The particles less than 50 μm contain the greatest concentration of heavy metals. On average, 69 ± 4% of the mass of each metal is present in the fraction less than 50 μm in diameter. The value is equal to 14.5 ± 0.8% for the 50–200 μm fraction and was less than 11 ± 2% for the fractions greater than 200 μm. Globally, 92 ± 5% of the metallic loads are consequently presented in the particles less than 50 μm that constitutes alone 84.5 ± 3.5% of the studied sediments, the metal sorption reactions are often rapid on clay minerals such as kaolinite and smectite [44]. The predominant association of the heavy metals with the fine fractions of the sediments has also

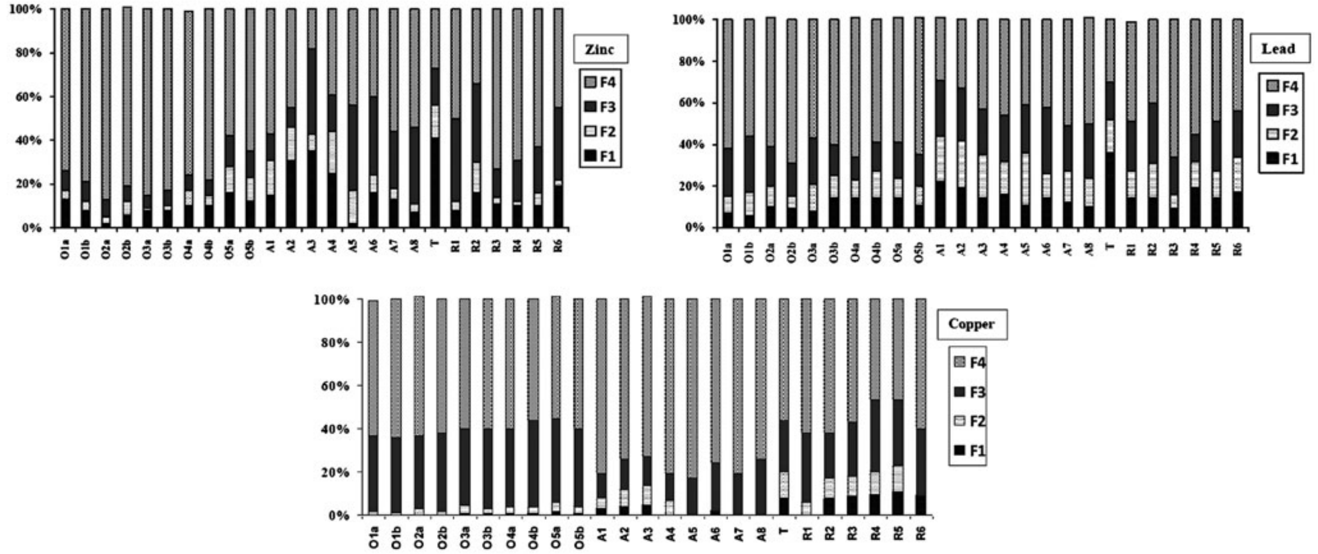

Fig. 2. Partitioning of Zn, Pb, and Cu in soils of mine (A) and the Tailling (T) of Assif El Mal mine, reservoir sediment (R), and river sediment (Oa = −10 cm; Ob = −20 cm) of studied Area among the four fractions of the sequential extraction.

Table 5
Mean concentrations of heavy metals (mg/kg SM) in the different granulometric fractions on all investigation stations ($n = 25$) (O: river sediment, A: mine soil, T: Tailing, and R: river sediment)

Fraction	Samples	Fraction (%)	Zn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Fe (mg/kg)
Clay and fine silt (0–20 microns)	O	20.7 ± 4.1	25.2 ± 3.5	9.6 ± 2.2	5.1 ± 0.9	1,440 ± 36
	A	68.4 ± 16.2	485 ± 21.6	44.6 ± 12	34.4 ± 12.5	1,235 ± 52
	T	22 .8 ± 6.5	1,512 ± 46	158 ± 22.5	61.4 ± 14.6	508 ± 37
	R	88.6 ± 15.3	1,775 ± 68	22.6 ± 3.4	5.2 ± 1.4	1,890 ± 78
Coarse silt (20–50 microns)	O	19 ± 7.2	22.7 ± 4.6	5.9 ± 1.6	2.3 ± 0.5	1,168 ± 27
	A	14.2 ± 3	234 ± 18.2	33.5 ± 8.5	28.6 ± 8.5	924 ± 39
	T	26.5 ± 4.6	1,108 ± 34	124.5 ± 18	52.8 ± 5.8	422 ± 31
	R	12.3 ± 2	612.8 ± 42	14.4 ± 3.8	3.4 ± 1.1	1,445 ± 64
Fine sand (50–200 microns)	O	28.6 ± 11.4	15.6 ± 3.2	4.4 ± 1.3	1.7 ± 0.4	472 ± 21
	A	7.2 ± 2	152 ± 14.6	16.4 ± 3.5	13.1 ± 4.6	614 ± 28
	T	31.3 ± 10.4	920 ± 38	132 ± 19	56.2 ± 12.5	472 ± 26
	R	6.3 ± 1.4	434.6 ± 31	7.8 ± 2.5	0.9 ± 0.06	908 ± 43
Sand coarse (200–2,000 microns)	O	31.7 ± 9.8	9.3 ± 2.5	3.5 ± 0.5	1.2 ± 0.2	310 ± 22
	A	10.2 ± 4	121 ± 18.6	12.3 ± 2.4	10.6 ± 2.6	510 ± 21
	T	19.4 ± 8.2	748 ± 92	126 ± 8.5	49.1 ± 8.2	441 ± 24
	R	3.6 ± 0.5	326 ± 36.5	4.4 ± 1.2	0.7 ± 0.09	711 ± 39
French soil standards			300	100	100	–

been observed many studies [18,45–48]. These results suggest high risk of water contamination. Lin et al. [47] have signaled that the potential toxicity to the aquatic ecosystem caused by the sediments which was caused by the fine sediments.

3.4. Mineralogical composition

The X-ray diffraction results of the sediment samples studied showed that quartz, muscovite, dolomite, and chlorite are the major minerals in these sediments.

Generally, we noted a common mineral matrix of quartz, dolomite, aluminosilicates (clinochlore, muscovite, and anorthite), and iron oxide (hematite) for all the samples of sediment reservoirs, mine soil, and tailing. Specific differences are the presence of goethite and illite in the tailing samples, and calcite in the reservoir sediment samples.

3.5. Physicochemical characterization of the water in the river and reservoirs of the studied area

Heavy metals in aquatic systems are removed from the water column by interacting with particulate or organic matter, and are deposited as sediments [47–50]. But, the heavy metals in the sediments might be released into the overlying waters again via various processes [51,52]. Also, however Sioud [53], have shown that the experiences of metal sorption (Cd, Cs, Ma, Co, and Zn) on natural particles of the Rhone are almost completely reversible after 72 days.

General water chemistry comprised of major anions and heavy metals is shown in Table 4. This data were used to understand the water contamination range of the mine sites. The most abundant anions are HCO_3^- and SO_4^{2-}, but all samples contained less than 60 mg/l of bicarbonates, with high concentrations of SO_4^{2-} (until 605 mg/l in water reservoirs). Nitrate compounds were also found in the waters sampled in reservoirs. These levels are probably being due to the oxidation and dissolution of sulfide minerals in tailings. However, a relatively low concentration of nitrate record in all water samples.

The pH values for the studied samples were consistently around 8 ± 0.2 with greater differences between the upstream and downstream of the valley. However, the electrical conductivities values for the reservoirs are significantly higher than that of the Oued water; they could reach 1809 ± 32 µs/cm.

Excepted Cu (3 mg/l), all the other metals are greatly exceeded the Moroccan Standards for Water Consumption (Zn = 3, Pb = 0.025, Fe = 0.2, and Ni = 0.02 mg/l) engendering the increases in the PI values to more than given tolerable level (PI = 1), specially in the water reservoirs and the station O_5 (with a values ranged from 1.25 to 1.88). Although, the concentrations of dissolved Cu and Ni are not high than those of Zn, the distribution profiles between the different stations showed a similarity which were characterized by an increase in the dissolved phase at water reservoirs and station O5, respectively, for Zn is 3.04 ± 0.32–5.98 ± 1.04 and 4.06 ± 0.42 mg/l (Table 6).

This increase of Zn and Pb in the reservoirs and the station O_5 was likely due to the fact that the waters of Oued Assif El Mal drained the mine tailings of the abandoned mine. Moreover, these stations are located in downstream of the mining excavation district of Assif El Mal corresponding to a mineralized zone or a deposit that are found galena, barite, chalcocite, chalcopyrite, pyrite, limonite, and goethite [15]. In this case, the drainage from this region leads to leaching of these elements in the waters of the Oued.

The statistical analysis, showed a highly significant ($p < 0.01$) correlation of Zn and Pb concentrations between the water and sediment of each station, with r-values are 0.74 and 0.83, respectively. For the other metals, positive correlations but not significant (at $p < 0.05$) were also obtained with r-values given as 0.32, 0.31, and 0.29, respectively, for Cu, Fe, and Ni. This was confirmed by another very good correlation highly significant ($r = 0.904$) between PIs and PIw. This will help to understand the nature of these metals and their species speciation in the aquatic environment.

4. Conclusion

Assif El Mal river draining its own mining site constitutes a representative example of the metal transfer from abandoned mine sites. This transfer of metal con-

Table 6
The chemical properties and concentrations of heavy metals in water samples

	pH	EC (µS/cm)	HCO_3^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)	Fe (mg/l)	Ni (mg/l)	PIw
O1	8.31	260	21.3	ND	50.2	ND	1.56	0.03	0.44	0.021	0.63
O2	8.23	288	23.2	2.93	41	ND	0.94	0.041	0.68	0.045	1.00
O3	8.11	282	13.6	1 .73	67	0.63	2.06	0.04	0.34	0.025	0.71
O4	8.2	320	20.1	1.2	69.5	0.56	2.86	0.052	0.82	0.023	1.06
O5	8.3	403	25.2	1.7	57. 6	0.94	4.06	0.055	0.90	0.024	1.25
R1	7.95	757.67	42.67	29.4	500.2	1.04	5.26	0.051	0.86	0.033	1.40
R2	8.08	1,532.33	43.60	33.13	311	0.86	3.04	0.048	1.24	0.0 31	1.46
R3	7.86	919.33	56.00	54.67	576.7	0.98	4.16	0.06	1.04	0.038	1.50
R4	7.79	1,592.33	52.13	63.12	595.2	1.3	5.11	0.057	1.53	0.034	1.88
R5	7.67	905.67	45.20	52.07	471.6	1.32	3.36	0.064	0.96	0.038	1.43
R6	7.78	1,809.00	51.87	52.82	605.4	1.14	5 .98	0.061	1.18	0.035	1.70
Guideline values	6.5–<8.5	2,700	–	50	250	2	3	0.01	0.3	0.02	

ND, not detected (lower instrumental detection limit).

taminants provides an indication of the destination and the metal sharing in the environment. In this paper, we have studied the physicochemical proprieties of the mine soils, tailing, and sediments. Also, the particle size classification and the heavy metals sequential extraction were analyzed. The general characterization of the sediments revealed that they were highly polluted with the heavy metals, and this pollution decreased exponentially with increasing distance from the mine. The total metallic concentrations exceed the French standards for several metals such as zinc, lead, or nickel.

The sequential extraction for the determination of metal speciation was a good alternative for total metal analysis in assessing the environmental risks of heavy metals in sediments. Large variability was observed among different samples studied and among different elements for metal speciation. On the other hand, the results of the first three binding forms in the sequential extraction, that represent a average percentages of the total metal content between 16.2 ± 5.8 and 81.15 ± 8.25% for Zn and 31.4 ± 6.6–70.25 ± 9.15% for Pb, are really reflected the pollution intensity of heavy metals related to the abandoned Assif El Mal mine, this contamination was showed by the value of PIs.

According to the grain size analysis, the sediment was principally textured by clays and fine loams. The analysis also showed that the heavy metals were predominantly associated with the fine particles less than 50 μm. These particles represent about an average of 70% in these studies samples.

Furthermore, the waters contained the high levels of Pb, Zn, Ni, and Fe that exceeds the Moroccan Standards for human consumption. Additionally, the PIw was more than the tolerable level (PIw > 1), particularly in water reservoirs. Finally, the best correlation between the PIs and PIw showed that the index pollution was a good alternative for total metal analysis in order to assess the risks of heavy metals, on the environmental and human health.

Since it is not possible to prevent these chemicals from draining into the drinking water sources and in an effort to combat the problem of reservoirs drinking water contamination by heavy metals in this rural area, rapid and significant treatment progresses is necessary. In this context, the many precautions as treatment flexibility and final efficiency, environmental security and friendliness, and low cost should be envisaged.

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