

## Heavy Metal Contamination of Soils and Water Resources Kettara Abandoned Mine

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**Abstract: Problem statement:** Metal mining; together with mineral smelting and processing, have contaminated the environment surrounding mine areas throughout the world exceeding natural background concentration. **Approach:** These processes introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids and solid wastes. The principal objective of this study was to investigate soil and water contamination in the vicinity of the kettara abandoned mine located in the South of Morocco. **Results:** High total concentrations of heavy metals were found in both tailings and soil samples. Furthermore in the tailings the maximum concentrations of the mobile fraction of metals were 76, 80 and 79 mg kg<sup>-1</sup> of Cu, Pb and Zn, respectively, for the soil samples the maximum concentrations values were 68, 52 and 26 mg kg<sup>-1</sup> of Cu, Pb and Zn, respectively. As a result of dispersion of the metals downstream and downslope, soils contained higher metal concentrations than those from nearby control sites (P<0.05). This may be due to surface runoff and strong wind action which caused the movement of mine waste material. The chemical properties of tailings were characterized by very low pH and high levels of EC. Furthermore, in the wet season the water from kettara mine contained elevated levels of Cu, Pb, Zn and SO<sub>4</sub><sup>2-</sup>. **Conclusion/Recommendations:** According to this study, the agricultural activity in the vicinity of the kettara mine requires careful consideration. Recultivation of the tailings and the remediation of surface water and soil are recommended.

**Key words:** Water contamination, tailings, soil, heavy metals, mobility

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### 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 waste water, provides obvious sources of contamination. Heavy metal contamination has been one of the 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 a 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 effects to human health (Fuge *et al.*, 1989) Mining and milling/beneficiation processes (crushing, grinding, washing,) generate four major categories of waste, i.e. (i) Mine waste (low-grade ore, overburden and barren rocks), (ii) Tailings, (iii) Dump heap leach and (iv)

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Acid mine water. These wastes are disposed in surrounding land and water in more or less environmentally acceptable manner.

Therefore, large areas of agricultural land can be contaminated. Morocco, for example, has a long history of metalliferous mining and the most extensive activities occurred during the early twentieth century. As a result, over 1000 metalliferous mines were distributed along mineralized zones; most of the mines were abandoned mainly due to economic reasons. Upon closure of the mines, mine waste materials, including tailings with elevated levels of toxic elements including As, Cd, Cu, Pb and Zn, 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. The principal objective of this study was to investigate soil and water contamination in the vicinity of the abandoned kettara mine located in the South of Morocco.

## MATERIALS AND METHODS

**Description of the area:** The studied mine are located 30km northwest of Marrakech in the core of the central Jebilet Mountains (Southern Morocco) Fig. 1 Hakkou *et al.*, 2008). The Kettara mine produced more than 5.2 Million tons (Mt) of pyrrhotite from 1964-1981 and was closed in 1982 (Hakkou *et al.*, 2008). During the exploitation, more than 3 Mt of mine wastes were stockpiled over an area of 16ha without concern for environmental issues. The ore contains minerals such as pyrrhotite, sphalerite, galena, chalcopryrite, pyrite, arsenopyrite and glaucodot. The mine was exploited for Cu, Fe and S. The large quantities of waste materials, including tailings, have been left untreated. Thus; these materials have been dispersed downslope both by surface erosion and wind action and by effluent draining the wastes into lower lying land used for growth of paddy rice and household garden crops.

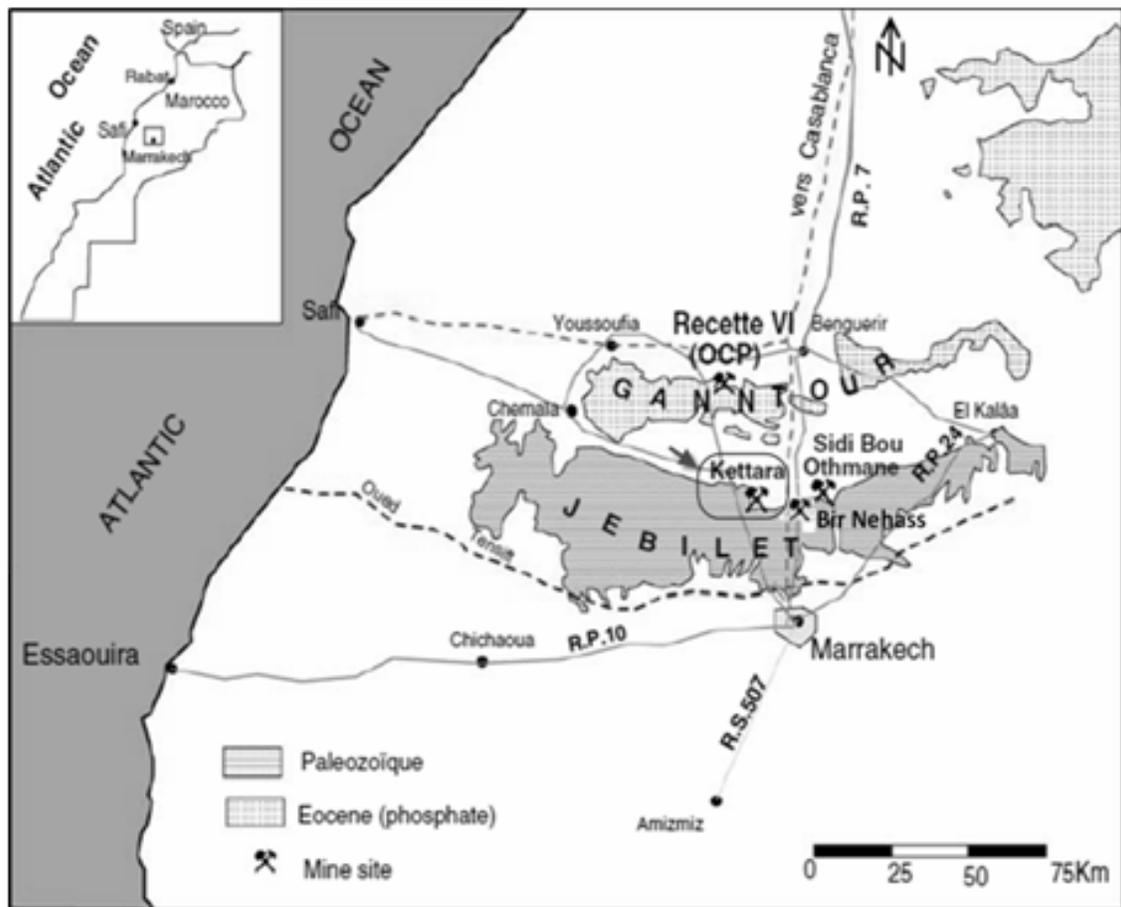


Fig. 1: Location of Kettara mine

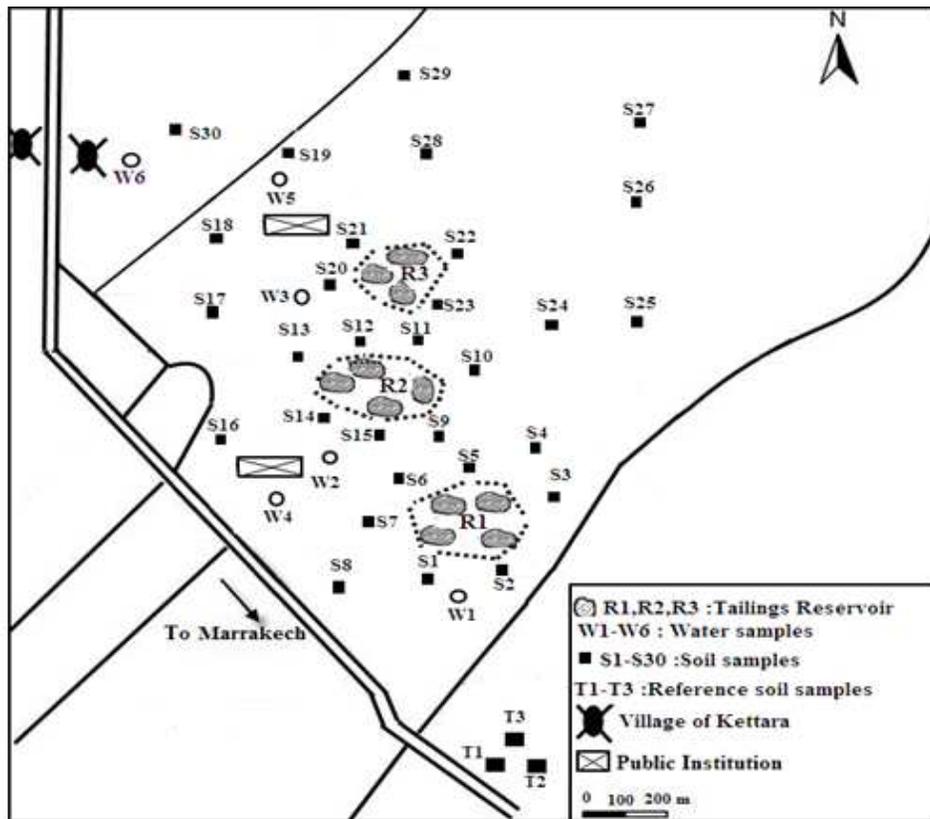


Fig. 2: Localization of the soil, the tailings and the water samples in and around the mine of kettara

**Soils and tailings analysis:** The samples of soil were taken from the upper 20 cm after removing the first layer of surface soil 2 cm within an area of 100 cm<sup>2</sup> per sample. Additionally 3 representative background samples, namely T1-T3, were collected 1 km far away from the mining site Fig. 2. Each soil sample comprised a composite of 9 subsamples. 4 Tailing samples were also collected as undisturbed core, by using a specially designed cylindrical stainless steel corer. Soon after collection, the soil and tailing samples were carefully transferred to clean and dry self-sealing polyethylene bags for transport 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 2 mm sieve. The tailing samples were thoroughly mixed and homogenized by coning and quartering, finally the soil and tailing samples were stored in tightly sealed polyethylene bags until further analysis.

The Physicochemical significant parameters of the soil and the Tailing samples such as pH values, Electrical Conductivity values (EC), Organic Matter (OM) and carbonate content were determined following the

standard analytical methods (Aubert, 1978). Total heavy metal concentration in soil and tailing samples was determined after digestion of the samples with microwave assistance. 0.5 g dry sample (100 mesh) was weighted in a PTFE digestion vessel and 3 mL HNO<sub>3</sub> (70%), 6 mL HCL (37%) and 3 mL HF (48%) were added. The digestion vessel was placed in the chamber of the microwave system (CEM MARS 5, Matthews, USA). After digestion, the sample solution was allowed to air-cool and then diluted with deionized water to 50 mL.

Mobility assays were performed by applying the established methodology (Perez *et al.*, 2008) consisting on sample extraction with HCl 0, 5 M at 1:5 ratio during 1h under magnetic stirring. After each extraction, the suspension was centrifuged and the supernatant was separated by filtering with 0.22 μm filter (Millex GS, Millipore and Ireland). The concentrations of Zn, Cu and Pb after total acid digestion and the resultant solutions of Mobility assays were determined by an Inductively Coupled Plasma Mass Spectrometer (Thermo Scientific XSERIES 2 ICP-MS). The isotopes <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>111</sup>Cd and the sum of <sup>206</sup>Pb+<sup>207</sup>Pb+<sup>208</sup>Pb were selected for the Determination

of the elements of interest. <sup>72</sup>Ge, <sup>115</sup>In and <sup>209</sup>Pb (each 100 µGL<sup>-1</sup>) were added to both the calibrated and sample solutions as internal standards to monitor and compensate for possible instrumental drift and matrix effects. Each experiment was conducted in triplicate and the results reported were the average values.

**Waters analysis:** Water samples were taken in and around the mine both in (dry and wet season) Fig. 2. The samples were filtered through 0.45 mm Millipore membrane filter. The pH; Total Dissolved Solid (TDS), Electric Conductivity (EC) and temperature of the samples were measured using a portable pH-TDS-EC meter. After acidification with concentrated nitric acid, the samples were stored in a cool box before chemical analysis. For anion determination, the filtered waters were directly stored in a cool box without acidification. Cu, Pb and Zn concentrations in acidified waters were determined by ICP-MS and the concentrations of HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in non-acidified waters were measured by Ion Chromatography (IC).

## RESULTS AND DISCUSSION

**Physical-Chemical properties of the soil and the Tailings samples:** The results obtained for pH, Electrical Conductivity (EC), Carbonate Content (CaCO<sub>3</sub>), organic matter and total metal concentration for the soil and Tailings Samples are summarized in Table 1.

The results obtained revealed that, in general, all samples of tailings have a very acidic pH ranged from 1.9-2.8 this low pH may be due to the weathering of sulfide minerals (pyrite (FeS<sub>2</sub>) and pyrrhotite (FeS) which join other metal sulfides: chalcopyrite (CuFeS<sub>2</sub>), glaucodot, galena and sphalerite have been observed but in very small proportions; a high electrical conductivity from 3000-3700 which means a high salt content, Organic matter content was mainly lower than 0.7% and a low concentration of carbonates (lower than 0.8%.) indicating that the nature of these tailings is not calcareous Table 1.

Table 1: Summary of pH, electrical conductivity (EC), carbonate content (CaCO<sub>3</sub>), organic matter (OM) and total concentrations of Cu, Zn and Pb for the soil and the Tailing samples taken at Kettara abandoned mine

Type	pH	EC (µS/cm)	CaCO <sub>3</sub> (%)	OM (%)	Cu (Mg/kg)	Zn (Mg/kg)	Pb (Mg/kg)
Tailing 1 (n = 4)	1.90	3700	0.41	0.60	1518.00	610	530
Tailing 2 (n = 4)	2.10	3400	0.67	0.64	1248.00	510	400
Tailing 3 (n = 4)	2.80	3000	0.77	0.68	780.00	230	100
S 1	3.90	1100	5.00	2.00	355.00	168	130
S2	3.70	1500	2.50	2.40	567.00	125	146
S3	3.40	1500	3.00	1.10	643.00	328	313
S4	4.70	970	4.50	2.10	281.00	51	120
S5	3.00	1500	4.00	1.75	772.00	145	310
S6	3.10	700	3.00	2.20	528.00	103	130
S7	5.10	1600	3.00	2.00	405.00	45	138
S8	7.70	100	2.00	2.40	98.00	26	81
S9	2.30	2300	2.00	2.00	814.00	406	349
S10	4.27	2100	2.10	2.30	487.00	171	134
S11	3.97	850	2.00	2.50	396.00	49	105
S12	4.02	670	4.00	2.60	424.00	60	106
S13	3.60	2100	3.30	2.90	987.00	47	133
S14	2.90	2350	5.00	1.40	1362.00	307	343
S15	2.85	2370	4.10	0.60	1347.00	101	101
S16	7.70	150	5.00	1.10	98.00	129	138
S17	7.60	180	3.00	1.40	61.00	28	87
S18	7.40	470	3.20	1.70	70.00	21	100
S19	7.90	120	4.00	1.05	65.00	38	90
S20	6.70	970	2.00	1.69	281.00	51	120
S21	6.20	1700	4.70	1.28	162.00	38	100
S22	7.34	520	2.30	2.00	242.00	44	121
S23	7.14	910	1.10	2.30	162.00	55	265
S24	7.70	180	3.50	2.50	53.00	25	82
S25	7.70	100	5.00	2.10	33.00	22	85
S26	7.60	100	5.30	2.30	38.00	28	77
S27	7.90	100	4.00	2.13	32.00	32	91
S28	7.30	70	3.00	2.53	27.00	27	77
S29	8.00	120	2.00	2.18	27.00	32	80
S30	7.30	70	2.00	2.02	27.00	43	61
Reference soil (n = 3)	8.12	60	3.10	2.84	29.00	13	55

In general, the 30 soil samples featured widely different soil properties. The Organic matter content was mainly lower than 3 % and ranged from 0.60 to 2.90%. The presence of a vegetation cover in some parts of the mining area, could explain the high values of OM content in some samples of soil.

The pH values showed a very broad interval, from alkaline soils to soils close to strong acidity: points located near the both tailing reservoirs R1 and R2 present a very acidic pH (2.30-5.10) compared to the reference samples with basic pH (pH = 8.12), the others sampling points have a basic pH very close to the reference sample .

The acidic pH is related to the phenomenon of oxidation of metal sulphides and iron sulphides such as pyrite and pyrrhotite in the tailings , Metal sulfides, especially Pyrites, can be oxidized easily under natural weathering conditions, resulting in large quantities of AMD generated and transferred into the surrounding environment through atmospheric dispersion and through the flow of water and release of metals from the ore and tailings because of the low acidity and high salinity of percolating solutions. This was one of the most important sources of heavy metals in the environment surrounding the mine.

The study area Promoted by a topography which causes a flow from north to south of the mine, the alkaline pH of soils in northern part (Tailing 3) of the mine can be explained by the intervention of topographical factors, because the Tailings reservoir is located at a higher level compared with samples of soils, which meant that theses soils does not undergo the same changes on the pH. The majority of samples taken around the tailing 1 and tailing 2 (tailing reservoir R1 and R2) present a high electric conductivity in comparison to the reference samples ( $60 \mu\text{s cm}^{-1}$ ). The electric conductivity in the nearest sites of R1 and R2 is ranged between  $670\text{-}2370 \mu\text{s cm}^{-1}$  Table 1. For the northern part (around the tailing reservoir R3) the electric conductivity is ranged between  $520\text{-}1700 \mu\text{s cm}^{-1}$ . It is observed to have a decreasing salinity gradient from the mining site to the far away points (S8, S16, S17, S19, S24, S25, S26, S27, S28, S29 and S30). The carbonate content mean Range is between 0.60-2.9%, the majority of the samples have carbonate content similar to those found in reference samples (2.80%).

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 (86/278/EEC, 1986) for the addition of sludge as amendment to agricultural soils, the maximum allowable concentrations of heavy metals

Cu, Zn and for agricultural soils is  $140,300$  and  $300 \text{ mg.kg}^{-1}$  respectively. The Tailings contained mostly Cu, Zn and Pb Table 1, the mean concentrations of Cu, Zn and Pb in tailing 1 (n = 4) were 1518, 610 and  $530 \text{ mg.kg}^{-1}$ , in tailings 2 (n = 4) 1248, 510 and  $400 \text{ mg.kg}^{-1}$  and in tailings 3 (n = 4) 780, 330 and  $100 \text{ mg.kg}^{-1}$  respectively. The metal concentrations in the tailings exceeded the European standards (Usero *et al.*, 2000; Hakkou *et al.*, 2006) for Cu, Zn and Pb in the tailing 1, in the tailing 2 and for Cu, Zn in the tailing 3.

According to the European standards (Kabata-Pendias and Pendias, 2001; 86/278/EEC, 1986) the majority of the soil samples located at the far away points of each reservoir of tailings (R, R2 and R3) showing values considered as background or tolerable levels for Cu, Zn and Pb. The soil samples taken around the area covered by mine tailing1 and tailings2 (S1, S2, S3, S5, S6, S7, S9, S10, S11, S13, S14 and S15) showed the highest values for all the metals, the maximum concentrations of heavy metals in soils around the tailing 2 were 1347, 406 and  $349 \text{ mg kg}^{-1}$  of Cu, Zn and Pb, respectively, around the tailing 1 the maximum values of heavy metals were 772, 328 and  $310 \text{ mg kg}^{-1}$  of Cu, Zn and Pb, respectively Table 1.

According to the European standards (Kabata-Pendias and Pendias, 2001; 86/278/EEC, 1986) the majority of the soil samples located around the tailing 1 and tailing 2 were classified into much polluted levels and exceed the maximum allowable concentrations of heavy metals Cu, Zn and Pb for agricultural soils.

**Contamination Factor (CF):** The CF is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background value (Eq. 1) (concentration in unpolluted soil) Table 2:

$$CF = (C_{\text{heavy metal}} / C_{\text{background}}) \quad (1)$$

The contamination levels may be classified based on their intensities on a scale ranging from 1-6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Muller, 1969).

**Pollution Load Index (PLI):** For the entire sampling site, PLI has been determined by the calculation of the product of the n CF (Eq. 2) (Usero *et al.*, 2000) Table 2:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (2)$$

where, n is the number of metals (n = 3 in this study) index provides a simple, comparative means for assessing the level of heavy metal pollution.

The Pollution Load Index (PLI) calculated from CF shows that the soils are moderately to heavily contaminate by investigated heavy metals Table 2.

The sampling Sites located around the tailings (S14, S9, S3, S5, S15, S1 and S2), shows the highest PLI more than 7 within the sampling Sites S4, S6, S7, S16, S12, S20 and S23) and the rest of the area is low to moderately polluted. Statistical analysis of the total metal concentrations showed a high significant correlation between metals in all the sampling points ( $P < 0.05$ ). This fact suggests the common origin of all the metals analyzed and, therefore, the mining activity can be pointed out as the source for the metal pollution of the studied area. The agricultural soils that are irrigated by mine drainage water contain very high levels of potentially toxic trace elements, although the total contents vary considerably depending on the location of the samples Table 1.

Two reasons may be suggested to explain the scattering of the metals from the mine area. Firstly, the physicochemical properties of the Kettara mine tailings Table 1, i.e., high heavy metal concentrations, low pH, low carbonates content, nature of the deposit: mine tailings contain sulfides which react with oxygen, generating a stream of acid water that also contains dissolved heavy metals and other minerals that can be transported to the mine surroundings by means of acidic drainage, aided by a topography which causes a flow from north to South of the mine. Secondly, wind transport of dust may be another important factor influencing the spreading of pollution. Previous study in the same site (Hakkou *et al.*, 2006) showed that runoff have an acidic pH ( $< 3$ ). This acidity favors the attack of the mineral content in discharges and release of contaminants in solution. According to these authors, this runoff is highly sulfated and has a very high salinity, resulting in a very high conductivity (Hakkou *et al.*, 2006)

Production of Acid Mine Drainage (AMD) in addition to decreasing pH, inevitably the leaching of various metals and high concentrations of sulfates (Hakkou *et al.*, 2006). In the reference area, however, the average concentrations of the metals are close to the world average of 30, 35 and 90 mg kg<sup>-1</sup> of Cu, Pb and Zn, respectively, reported by (Bowen, 1979). There is a statistically significant difference between metal concentrations in the contaminated and reference soils ( $P < 0.05$ ).

**Mobility of Cu, Pb and Zn in soil:** Once detected the most polluted samples of soil, a real evaluation of their potential risk can be obtained from the results of metals mobility, by using the single extraction procedure, the concentrations of heavy metals in soils extracted by the HCl 0, 5 M solution are shown in Table 3.

Table 2: Calculation of the Contamination Factor (CF) and the Pollution Load Index (PLI) for the soil and the Tailing samples taken at Kettara abandoned mine

Type	Cu CF	Zn CF	Pb CF	(PLI)
Tailing 1(n = 4)	52.00	46.92	9.63	28.64
Tailing 2(n = 4)	43.03	39.23	7.27	23.07
Tailing 3 (n = 4)	26.90	17.69	1.81	9.51
S 1	12.24	12.92	2.36	7.20
S2	19.55	9.62	2.65	7.93
S3	22.17	25.23	2.69	11.46
S4	9.69	3.92	2.18	4.36
S5	26.62	11.15	5.63	11.87
S6	18.21	7.92	2.36	6.98
S7	13.97	3.46	2.50	4.94
S8	3.38	2.00	1.47	2.15
S9	28.07	31.23	6.34	17.71
S10	16.79	13.15	2.43	8.13
S11	13.66	3.77	1.90	4.61
S12	14.62	4.62	1.92	5.06
S13	34.03	3.62	2.41	6.67
S14	46.97	23.62	6.24	19.05
S15	46.45	7.77	1.83	8.71
S16	3.38	9.92	2.50	4.38
S17	2.10	2.15	1.58	1.93
S18	2.41	1.62	1.81	1.92
S19	2.24	2.92	1.63	2.20
S20	9.69	3.92	2.18	4.36
S21	5.59	2.92	1.81	3.09
S22	8.34	3.38	2.20	3.96
S23	5.59	4.23	4.81	4.84
S24	1.83	1.92	1.49	1.74
S25	1.14	1.69	1.55	1.44
S26	1.31	2.15	1.40	1.58
S27	1.10	2.46	1.65	1.65
S28	0.93	2.08	1.40	1.39
S29	0.93	2.46	1.45	1.49
S30	0.93	3.31	1.11	1.51

Table 3: The mobility of Cu, Pb and Zn in the most contaminated samples of Kettara (mg kg<sup>-1</sup>)

Type	Cu		Pb		Zn	
	Total	Mobile	Total	Mobile	Total	Mobile
Tailing1	1518	76	610	49	530	80
Tailing 2	1248	62	510	41	400	60
Tailing3	780	39	230	18	100	15
S 1	355	18	168	13	130	20
S2	567	28	125	10	146	22
S3	643	32	328	26	313	47
S5	772	38	145	12	310	46
S6	528	26	103	8	130	19
S7	405	20	45	4	138	21
S9	814	41	406	32	349	52
S10	487	24	171	14	134	20
S11	396	19	49	4	105	16
S12	424	21	60	5	106	16
S13	987	49	47	4	133	20
S14	1362	68	307	25	343	52
S15	1347	67	101	8	101	15
S20	281	14	51	4	120	18
Reference soil	29	Nd	15	Nd	55	4

ND, not detected (lower instrumental detection limit)

The maximum concentrations of the metals were found in the tailings sites (R1-R3) Fig. 2 with up to 76-49 and 80 mg kg<sup>-1</sup> of Cu, Pb and Zn, respectively. For

soil samples the maximum concentrations of mobile fraction were found in the soil around the tailings (R1-R3) with were 68-32 and 52 mg kg<sup>-1</sup> of Cu, Pb and Zn, respectively, this Mobility assays indicates also that the mobile fraction present about 15% of Zn, 10% of Pb and 5% of Cu in the soil samples; this indicated that the mobility Zn and Pb was high than that of Cu and we know that the bioavailability and eco-toxicity of metals mainly depends on their speciation in soil.

However, were relatively low in a nearby control area with, the results indicate that there is a statistical difference between average metal concentrations in the contaminated and reference soils (P<0.05).

In general Heavy metals in soil are distributed in 4 fractions: the mobile fraction, the reducible fraction, the oxidizable fraction and the residual fraction, the mobile fraction and the reducible fraction are readily to be absorbed in plants or in water system causing pollution. So, these fractions should be identified as direct effect fraction. Because the all the soil samples analyzed for Mobility assays are acidic and located in AMD area, the soil has highly oxidizing property.

The oxidizable fraction in this oxidizing condition is easily mobilized and transformed into mobile fraction or reducible fraction, potential of that eco-toxicity should not be ignored. So, the oxidizable fraction can be identified as potential effect fraction.

The heavy metal bound to residual fraction is often considered “unreactive” and not affected by environment changes, is identified as stable fraction. Therefore, it could be inferred that the potential environmental impact of heavy metals in soils was related not only to their total concentrations and chemical forms, but also could increase with time depending of pH, EC and the content of organic matter.

**The chemical properties and concentrations of Cu, Pb and Zn in water samples:** The chemical properties and the concentrations of Cu, Pb and Zn in water waters are shown in Table 4. The pH values was found being lower in mine waters (W1-W3) located nearest the tailings (R1-R3) the pH values were ranged from 2.60-5 for waters taken in dry season and from 2.20-4.10 in wet season, the pH in waters samples (W4-W6), located to the far away points of the tailings was higher than 7.12.

The relatively low water pH of mine waters may be due to the dissolution and decomposition of sulfide minerals including pyrite in mine waste dumps tailings. Total Dissolved Solid (TDS) give information on the total cations and anions in waters. Because effluent draining the mine wastes contained elevated levels of those ions, the maximum TDS of water samples in the effluent was 980 m L<sup>-1</sup> sampled in the dry season and 1185 m L<sup>-1</sup> sampled in the wet season, Electric Conductivity (EC) is positively correlated with TDS. The highest EC was found in effluent draining from the mine wastes with 2700 μS cm<sup>-1</sup> sampled in dry season and 3280 μS cm<sup>-1</sup> sampled in wet season. TDS, EC and concentrations of metals in waters decreased with distance from the tailings.

In general, metal concentrations in natural waters are very low due to their low solubility in the aquatic environment. According to (Bowen, 1979), fresh water contains 3.0, 3.0 and 15 m/L of Cu, Pb and Zn, respectively. However, tens to hundreds of times these concentrations of the metals can be found in waters contaminated by various sources (Fergusson, 1990). The concentrations of Cu, Pb and Zn in water samples are also shown in Table 3. High concentrations of heavy metals were found in mine waters taken in the wet season, with maximum contents of 1.90, 4.15 and 33.00 m L<sup>-1</sup> of Cu, Pb and Zn, respectively. These concentrations may be derived from interaction of rain with tailings containing elevated levels of these metals. Heavy metals from acidic tailings with sulfide minerals can be extracted by large amounts of rain, especially in the wet season.

Thus, they can be continuously discharged downstream and decreased exponentially with distance from the mine.

The dispersion patterns of these metals varied depending upon their solubility and mobility in the aquatic environment. In general, Zn with higher mobility can be widely dispersed downstream and Cu and Pb with lower solubility can be dispersed only to the area adjacent to the tailings.

Table 4: The chemical properties and concentrations of Cu, Pb and Zn in water samples

Sample ID	Samples in dry season						Samples in wet season					
	pH	TDS (mg/l)	EC (μS/cm)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)	pH	TDS (mg/l)	EC (μS/cm)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)
W1	2.60	980.0	2700.0	0.70	18.8	0.30	2.20	1185.00	3280.0	1.90	33.00	4.15
W2	4.70	350.0	549.0	0.44	6.70	0.20	3.90	379.00	615.0	1.23	15.96	2.85
W3	5.00	288.0	479.0	0.28	4.71	0.12	4.10	295.00	513.0	0.93	12.85	0.50
W4	7.45	8.7	16.0	0.02	ND	ND	7.12	13.15	21.5	0.02	ND	ND
W5	7.76	9.0	16.7	0.02	ND	ND	7.50	22.18	19.0	0.02	ND	ND
W6	7.67	8.0	14.7	0.01	ND	ND	7.21	18.00	18.0	0.02	ND	ND

ND, not detected (lower instrumental detection limit)

Table 5: The concentrations of some anions in waters in and around the kettara mine (mg.kg<sup>-1</sup>)

Sample ID	Samples in dry season			Samples in wet season		
	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
W1	0.00	9.40	1200	12.00	7.12	4200
W2	9.85	4.74	1100	3.90	3.12	2800
W3	21.03	3.58	1010	4.10	2.78	1589
W4	14.52	ND	325	7.12	1.50	680
W5	26.90	ND	311	7.30	1.00	512
W6	44.10	0.05	155	24.52	3.00	241

ND, not detected (lower instrumental detection limit)

**Anion concentrations in waters samples:** The concentrations of HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in water samples are shown in Table 5: All the samples contained less than 45 mg l of bicarbonates, High concentrations of SO<sub>4</sub><sup>2-</sup>, over 1000 mg/L, were also found in the waters sampled in both the dry and wet seasons (waters around the tailings). These levels are likely to be due to the oxidation and dissolution of sulfide minerals in tailings. However, the concentrations of NO<sub>3</sub> in all the water samples were relatively low.

### CONCLUSION

The principal objective of this study was to investigate soil and water contamination in the vicinity of the abandoned kettara mine located in the South of Morocco. This investigation was based firstly on the determination of total concentration of several heavy metals (Pb, Zn, Cu) in both soil and water (dry season and wet season) by ICP-MS, secondly on the determination Mobility of Pb, Zn and Cu in the most polluted soil and tailings samples by using the single extraction procedure with solution of HCl 0, 5 M), finally on the determination of some anions (HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) in water taken in and around the mine both in dry season and wet season by Ion Chromatography (IC). In this study of an area around the abandoned kettara mine, soils and waters have been contaminated by past mining activity. High concentrations of heavy metals extracted by acid digestion were found in tailings with maximum values Cu (1500 mg.kg<sup>-1</sup>), Pb (510 mg.kg<sup>-1</sup>) and Zn (650 mg.kg<sup>-1</sup>). A high total concentration of heavy metals was also found in soil samples with maximum values, Cu (1347 mg.kg<sup>-1</sup>), Pb (349 mg.kg<sup>-1</sup>) and Zn (406 mg.kg<sup>-1</sup>).

Furthermore in the tailings the maximum concentrations of the mobile fraction of metals determined by extraction in 0.5N HCl were 76 , 80 and 79 mg.kg<sup>-1</sup> of Cu, Pb and Zn, respectively, for the soil samples the maximum concentrations values were 68,

52 and 26 mg.kg<sup>-1</sup> of Cu, Pb and Zn, respectively, this Mobility assays indicates also that the mobile fraction present about 15% of Zn, 10% of Pb and 5% of Cu in the soil samples; this indicated that the mobility Zn and Pb was high than that of Cu .

Pollution Load Indices (PLIs) derived from contamination factors show that all sampling points around the tailings reservoir area exceed unity and may be considered as highly polluted sites. Lower values for pH and higher levels of TDS and EC are found in waters sampled immediately downstream of effluents passing through tailings. Furthermore, high levels of heavy metals are found in the water. Thus, it can be understood that the main source of heavy metals in waters is the tailings containing elevated levels of the metals. In addition, over 1000 mg L<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup> is also found in the effluents, mainly due to leaching and oxidizing of sulfide minerals including pyrite, arsenopyrite, galena and sphalerite in tailings. Like dispersion patterns of soils, heavy metal concentrations in waters exponentially decreased with increasing distance from the tailings and they reach background levels at 1 km downstream. Tailing dumps have mainly a local impact and it is most likely that the activity of wind does not contribute significantly to contamination of surroundings. The higher heavy metal content in close proximity to the tailings is likely due to leaching and surface runoff.

The latter is a consequence of an inadequate deposition of the waste material .Shows the fate and impact of the tailing dump. The leachate of the tailing dump may contaminate the soil and groundwater. Surface runoff increases the heavy metal content of top soil, surface water and indirectly, the tissues of plants.

All these elements are receiving environment surrounding the mine abandoned Kettara, an area with a high risk of metal pollution that can affect water, soil, fauna, flora and undoubtedly human health of the area nearest and around the mine of kettara. Hence the importance of providing substantial efforts to develop methods of restoration and remediation cost-effective.

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