



Research article

Hydrogeochemical assessment of mine water discharges from mining activity. Case of the Haut Beht mine (central Morocco)

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Abstract: The rocks are likely to give a geochemical signature to the groundwater circulating there. Therefore the hydro geochemistry of the mine's water is influenced by the mining method. The continuous pumping of the mine water gives discharges that induce harmful impacts on the environment. The Sebou basin is subjected to strong industrial and urban pollution, but in the literature, the evaluation of the mining impact on this area is neglected. This paper is dedicated to this issue and as part of the evaluation of the mining impact on the Sebou watershed, the haut Beht mine was chosen among the four mines which include the watershed, and then we proceeded, as the purpose of this work, to evaluate the physicochemical quality of this mine's water discharges and their metallic trace elements (MTE) load (As, Pb, Cd, Zn, and Cu) through monitoring of four locations during two analysis campaigns in 2014 and 2015. This monitoring was performed by ICP-MS analysis. The results showed absenteeism of the acidic nature of mine's water, characterizing acid mine drainage (AMD). The majority of the analyzed water presents important concentrations of sulfate. During the 2014 campaign, the examination of trace metal element concentrations showed, at station 2, contamination of Iron, Aluminum, Manganese and, Arsenic. However, the concentrations of Pb, Cd, Zn, and Cu elements remain conform and very low compared to the limit of standards. The monitoring of the overtake elements made it possible to identify the degree of contamination of the mine's water discharges and to note an improvement in time in the mine water discharges quality.

Keywords: Sebou River; Environment; metallic trace elements; mine water; discharges

1. Introduction

The interest of evaluating the impacts of mining and its wastes on the environment did not arise until the 1990s. This interest required, in several countries, the implementation of mining activities regulations to limit the risks of pollution and to preserve natural ecosystems. Like in other countries, the mining sector in Morocco has found itself confronted with this environmental issue. The mining regulations (law 33-13) aim to set a range of new conditions for mining, taking into account the environment parameter during all phases of exploitation and post-mine. However, the problem of old mines exploited and abandoned without rehabilitation still remains [1,2].

Mining generates negative impacts on the environment as a result of direct or indirect effects during activities and/or after the closure of the mine [3,4]. Freshwater basins are the most affected element by such activities due to the water usage for the ore treatment and mine water discharges [4]. Thus, mines are increasingly threatening the water resources on which the whole ecosystem depends. Water is then considered as a "victim of mining" [5]. Metals are omnipresent in surface and ground waters, and their concentrations are generally very low, hence comes the name "metallic trace elements (MTE)". Mineral deposits are concentrations of metallic or other mineral commodities in the Earth's crust that result from a variety of complex geologic processes. The natural weathering and erosion of a mineral deposit at the Earth's surface disperse their constituents into the waters, soils, and sediments of the surrounding environment [6,7]. Thereby, the exploitation of a deposit rich in metals generates a change in terms of the quality of the water in contact with the mining works [8]. Around the world, several previous studies have been devoted to the problem of the abandoned mines' impact on the environment [2,9–17]

The present work falls within the general perspective of understanding the pollutants behavior and the metallic trace elements mobility in the mining environment, through the diagnosis of the current contamination situation and its evolution over time. The aim of the work is to ensure the protection of the environment against the nuisance caused by mining activity in the study area. The Haut Beht mine is located at the Beht watershed which is part of the Sebou watershed (sub-basin) (Figure 1). The Sebou River drains one of the main watersheds of Morocco in terms of water resources. However, it is subjected to a strong pollution [18–21]. The waters of Sebou have been experiencing a significant deterioration in their quality for several years, due to domestic and industrial discharges [22–25]. The Sebou watershed contains 13.3% of the country's industrial units, 7% of which are located in the Fez region, 3.2% in the Meknes region, and 3.1% in the Kenitra region [18]. In several previous studies, water pollution in the Sebou basin and its sub-basin Beht has been treated, among these studies we can cite [18–24]. for the Sebou and [25–28]. for The Beht, but to our knowledge there is no study that has been dedicated to the evaluation of the mine water discharges quality and their impact on the environment like this work.

The purpose of this work is to evaluate the physicochemical quality of the Haut Beht mine water discharges and their metallic trace elements (MTE) load (As, Pb, Cd, Zn, and Cu) through monitoring of four stations during two analysis campaigns in 2014 and 2015. The mine water which is considered in other studies as natural mine discharges, because when the continuous pumping of the water from the mine stop in the abandoned mines, its mine water infiltrates and becomes more

charged in the mine, achieving by gravity the underground waters and contaminating it by heavy metals. The mine water discharges are originally from the mine, and they are different from those coming from the mine tailing dam which is treated in several studies as the only mine' discharge. The evaluation of the mine water load in trace metal element and other analyses in this work are elaborated in the world for cases of sustainable management of mine water discharges and the reduction of their environmental impacts, or in the context of the performance monitoring of a treatment station of mine water discharges, or for post-mine monitoring and impact assessment (Table2).

2. Materials and method

2.1. Presentation of the study area

2.1.1. Geographic and hydrological context

The study area is in the Beht watershed (sub-basin of the sebou watershed: The watershed of the river Beht is located northwest of Morocco and occupies the southwestern part of the Sebou basin), which is bounded on the north by the Gharb plain and the Meknes plateau, on the south by the Oum-Erbia basin, on the west by the Bouregreg watershed and on the east by the Middle Atlas, which occupies the southwestern part of the Sebou watershed in northwestern Morocco [29]. The administrative territory of the Beht watershed overlaps contains five provinces and twenty-six Rural Communes (Figure 1). The study area has a mountain character, and does not contain a generalized groundwater table. The water resources of the localized water tables are used in the form of springs or by wells in the alluvium by the local populations for the irrigation of small plots or the supply of drinking water. In addition, there are alluvial aquifers along the Beht river where small perched aquifers with low flow rates are found. The HBM mine is located on the boundary of Beht river, The main affluent of the Sebou river, and its two affluents 1 and 2 (Figures 1 and 3). The Sebou watershed covers an area of 40,000 km² located between the meridians 3°50' and 6°40' W and the parallels 33° and 35° N. This watershed, which includes 1/3 of Morocco's surface water resources, is drained by the Sebou river that originates in the Middle Atlas and travels about 500 km before reaching the Atlantic Ocean near Kenitra [30]. The watershed of Sebou is the richest in terms of water resources in Morocco, with water supplies of the basin amounting to more than 5 billion m³/year, and it is one of the regions with the most important potential of irrigable and irrigated lands and industries at the national level. All these activities affect the quality of waters in this basin and cause more or less significant changes to the living communities [22,24,31].

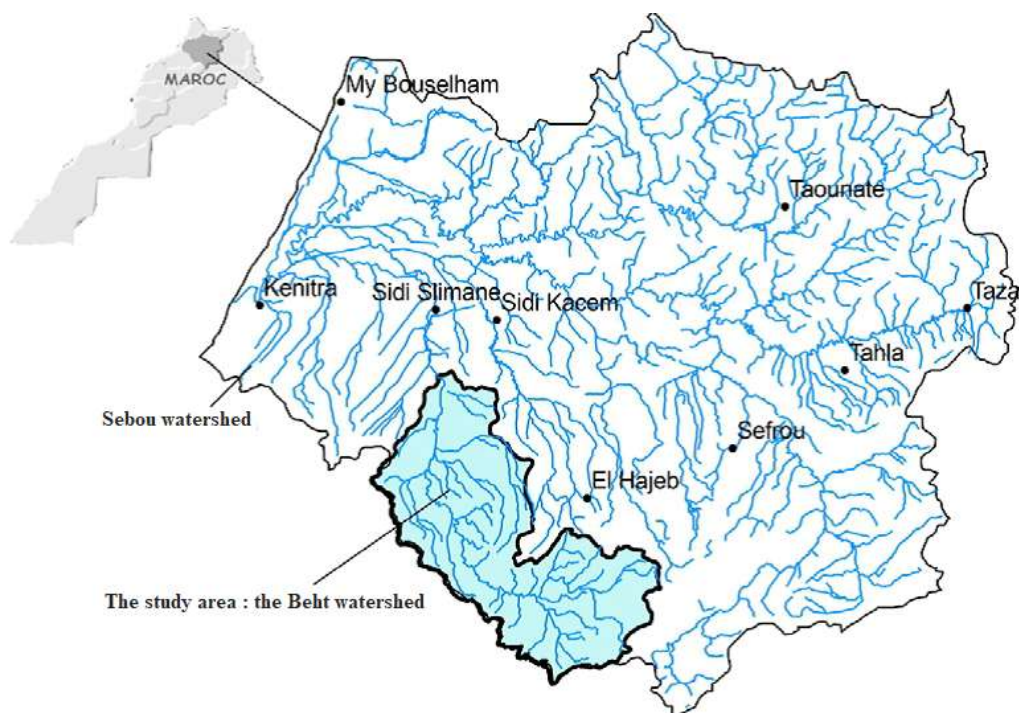


Figure 1. Geographical location of the study area: the Beht watershed in the context of the Sebou watershed [25].

2.1.2. Geological and hydrogeological context

From a geological point of view, the mine studied is located in the north-eastern part of the massif of central Morocco, which is a northern zone of the western Meseta [32,33]. This zone consists essentially of a Neoproterozoic substratum (acid or intermediate lava and low flush granites) [34,35], a Paleozoic cover (Cambrian to Permian age) and sedimentary and volcanic Meso-Cenozoic cover [2,32,33,35,36]. The main Paleozoic formations of the mine are: micro-conglomeratic schist, Ordovician quartzite (Ashgill), and Black Silurian graptolite shale (Gothlandian) [37,38]; yellow tentaculite schist is associated with sandstone banks and Devonian seedy limestone formations [38] (Figure 2). The mine is located in a dislocation zone of the Smaala-Oulmes (NE-SW) major fault, which ends at the NE with several branches of the same direction and shows NNE-SSW branches [38–41]. The system of this fault is truncated further to the north by the Tafoudeit accident overlapping the Namur formations and the Visean lands [37,38,42].

The mineralogical study in different areas of the massif of central Morocco made it possible to distinguish different types of ores, as breccia pyrite brecciated ore, massive ore with pyrrhotite, pyrite milky ore, and ribbon ore with pyrrhotite and chalcopyrite. The mineral paragenesis is dominated in some areas by pyrrhotite (more than 90%) with pyrite, chalcopyrite, magnetite, and glaucodot (Co, Fe) which are all associated. On the other hand, sphalerite, galena, and arsenopyrite are present in accessory quantities [43–48]. The regional geological framework has given mineral richness to the Sebou watershed, which includes four deposits (active and abandoned) [2,49,50].

The study area does not contain a generalized groundwater table. The water resources of the localized water tables are used in the form of springs or by wells in the alluvium by the local

populations for the irrigation of small plots or the supply of drinking water. In addition, there are alluvial aquifers along the Beht river where small perched aquifers with low flow rates are found. Taking into account the predominance of schistose and marl formations that form the watershed of the Beht river, it seems certain that the Groundwater availability in the Beht Basin remains very low. The existence of some auriferous rocks, with low water productivity and very limited extension, is mainly related to secondary modifications affecting the initially impermeable formations, to which are added appropriate structural forms (faults) [51].

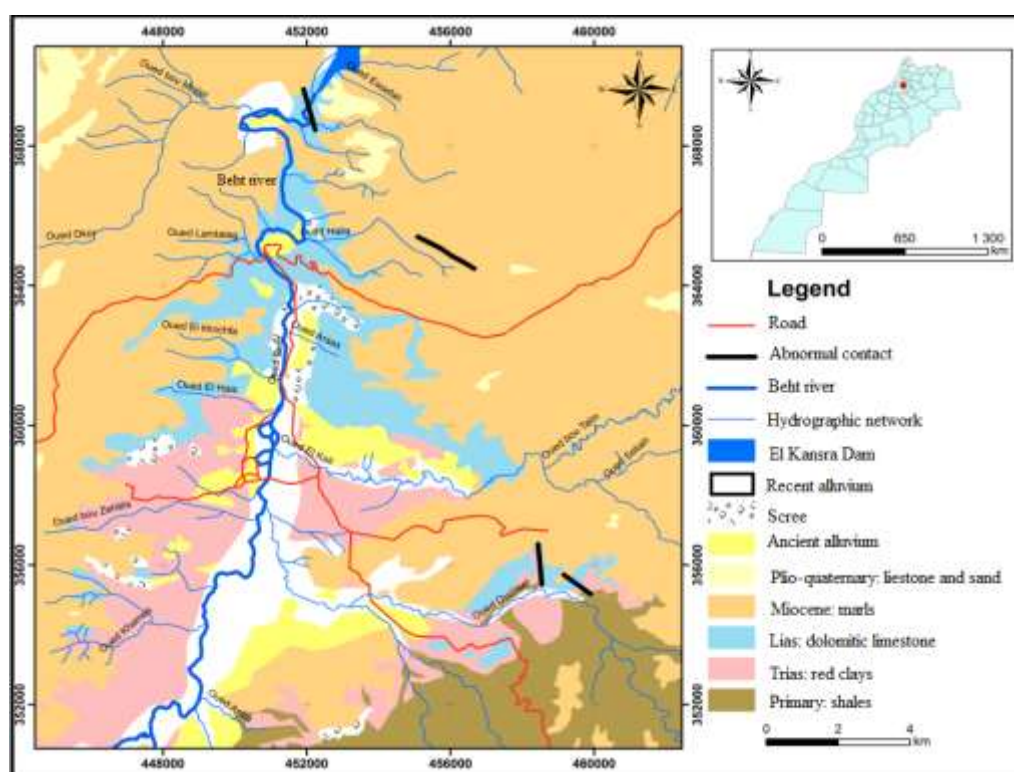


Figure 2. Geological map and structural domain of the Moroccan Hercynian central massif [52].

2.1.3. Climatic context

From a climatic point of view, the mine is located in the Beht watershed, the region's climate is a Mediterranean type with oceanic influence and becomes continental inland [25]. It is manifested by rainy winds coming from the west and decreases in precipitation away from the sea and in protected valleys like those of Beht or high Sebou before increasing rapidly on the slopes of the Rif. These influences of altitude, latitude, and exposure are combined to form a local microclimate where cold, frost, snow, and winter rains can oppose summer heat and thunderstorms [53,54]. The rains are poorly distributed throughout the year and very irregular from one year to the next. Average annual temperatures in the watershed range between 15 °C and 19 °C depending on altitude and continentality summer temperatures are high, the hottest months are July and August with average highs of 34 to 36 °C and the coldest months are December, January and February. The average of the minima is 3 to 7 °C [29]. The annual average rainfall in the basin is 600 mm on average with a maximum of 1000 mm on the heights further northward and a minimum of 300 mm [53].

2.1.4. Soil type

The soil cover of the Beht watershed is essentially characterized by soils whose chemistry is dominated by the presence of varying amount of alkaline earth (calcium and magnesium) because of the limestone backbone of the area [55]. The lands of the Beht watershed are limestone clay-loam in nature, the upper horizons of which are relatively rich of organic matter. They are formed on the recent and sub-current alluvial deposits of the Beht river. The porosity is medium, and the compactness is quite high. Structural stability of water is precarious, and under the effect of excess water (irrigation, rain), the upper horizons become crusty (beating soil) [56].

2.2. Sampling stations

In the context of the study of the impact of mining activity on the environment at the Sebou watershed that we chose the haut beht mine (HBM) among the four (active and abandoned) mines that include the Sebou watershed [2,49,50], and we proceeded to a physico-chemical characterization of its mine's water discharges and an assessment of their load in metallic trace elements and their potential and punctual impact on the environment, through two sampling and analysis campaigns, in 2014 and 2015 at the four discharge points of the mine's water.

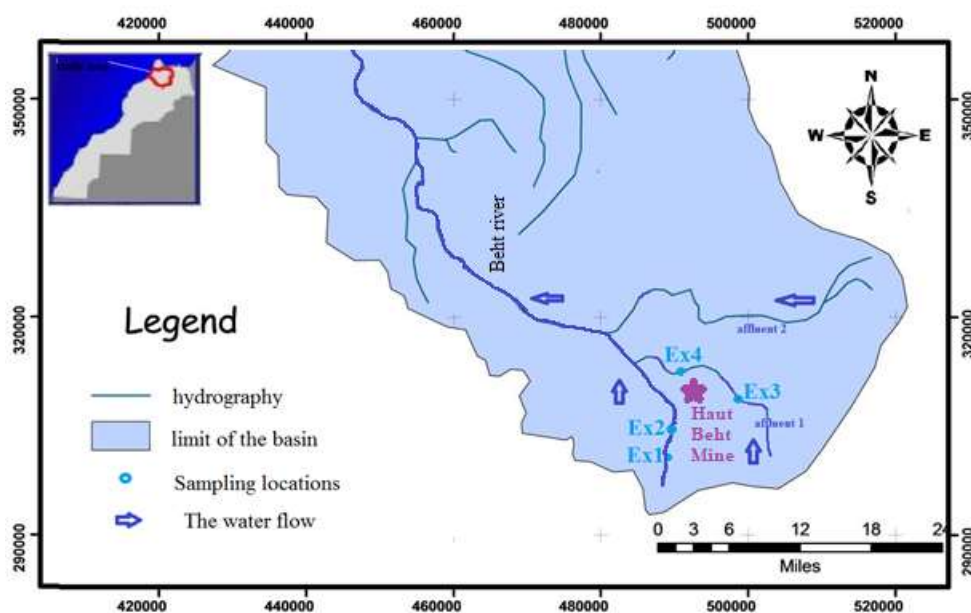


Figure 3. Map of the location of the study area and the four sampling stations.

The sampling stations were chosen to assess the physico-chemical quality and the trace metal load of the mine's water discharges. At the four selected stations, four water discharge samples were taken during two sampling and analysis campaigns carried out in 2014 and 2015 (Figure 3).

- Station 1: (Ex 1): the water discharge of the station 1 is located upstream of all other discharge points on the Beht river.
- Station 2: (Ex2): the water discharge of the station 2 is located downstream the station 1 (Ex1) on the Beht river.
- Station 3: (Ex3): the water discharge of the station 3 is located upstream of the discharge

point of Ex4 on the same affluent of the Beht river, affluent 1.

- Station 4: (Ex4): the water discharge of the station 3 is located downstream the discharge point of Ex3 on the same affluent of the Beht river affluent 1.

2.3. Methods of analysis

The mine water discharges samples were taken in 2014 and 2015 at the four sampling stations. Sterilized polyethylene vials were used for sampling, and each sample was taken to avoid the degassing of the sample, then to do this each bottle is filled gently while minimizing the effects of turbulence. Hermetically sealed, sample vials are stored at 4 ° C for rapid transport to the analytical laboratory in order to avoid changes in chemical composition due to degassing and photo-lytic or microbial reactions. Water discharges samples were acidified by the addition of 4% nitric acid to avoid changes in MTE concentration.

Following standardized methods (Table 1), 19 variables were monitored physico-chemically, including two in situ (pH, temperature).

The heavy metal analyzes were performed by ICP-MS (inductively coupled plasma mass spectrometry), which is a highly sensitive technique with detection limits up to part per trillion (ppt) (ng / l), for monitoring the evolution of the metal charge of water discharges in five particular elements: Lead (Pb), Zinc (Zn), Copper (Cu), Cadmium (Cd) and Arsenic (As).

The two sampling and analysis campaigns of water discharges (C1: 2014 campaign and C2: 2015 campaign) were carried out by a state-approved laboratory. The samples were taken following the AFNOR standard NF EN 25667 (ISO 5667) (table 1).

Table 1. The references of the basic analytical methods adopted by the analytical laboratory.

TESTS	REFERENCE METHODS	TESTS	REFERENCE METHODS
Accredited tests in chemistry	Accredited tests in chemistry		
pH	NF T 90-008 / NMISO10523	As	FD T 90-119
T °C	NF EN 25667 (ISO 5667) /NM 03.7.008	As	NF EN ISO 11885
Sulfates	NF T 90-040 / NM ISO 9280	Al	NF EN ISO 11885
Pb	FD T 90-112	Al	FD T 90-119
Pb	FD T 90-119	Zn	FD T 90-112
Pb	NF EN ISO 11885	Zn	NF EN ISO 11885
Cd	NFENISO5961	Cu	FD T 90-112
Cd	NF EN ISO 11885	Cu	NF EN ISO 11885
Fe	FD T 90-112	Cr	NF EN1233
Fe	NF EN ISO 11885	Cr	NF EN ISO 11885
Mn	NF EN ISO 11885	Sb	NF EN ISO 11885
Mn	FD T 90-112	Ni	FD T 90-119
Co	NM 03-7-022	Ni	NF EN ISO 11885
Co	NF EN ISO 11885	Se	NF EN ISO 11885
Sn	NF EN ISO 11885	Se	Se FD T 90-119
Ag	NF EN ISO 11885		

3. Results and discussion

3.1. Physicochemical characterization and metallic load of the mine water discharges

The exploitation of deposits rich in sulfides [43–46,57] expose rocks to the action of air and water which together have a strong oxidizing power. Oxidation of pyrite, and other associated primary minerals in sulfide deposits, results in mine water characterized by significant amounts of sulfates and dissolved heavy metals. [58]. The heavy metals chosen in this study are linked to sulfides because the arsenopyrite is the main source of arsenic (As), the Chalcopyrite contains most of the copper, the Zn and Cd are in sphalerite [8,59], and since the native lead (Pb) is rare, and due to its chalcophile nature, it is associated with sulfide deposits [8,47,48].

All of the analysis' results of the eight samples of the mine water discharges collected during the 2014 and 2015 campaigns were compared with the general limit values for discharges into surface or underground water. The analysis of the results obtained made it possible to identify the pH variability, which is a feature key of acid mine drainage (AMD), as well as the elements in excess and the elements relating to the metallic load of water discharges, in particular lead (Pb); Zinc (Zn); Copper (Cu); Cadmium (Cd) and Arsenic (As).

3.1.1. pH

The pH varies between 7.6 and 8.35 during C1 and between 7.6 and 8.2 during C2 (Figure 4). The upstream/downstream spatial distribution of the sampling stations shows a low variability of the pH values recorded during the C1 and C2 campaigns.

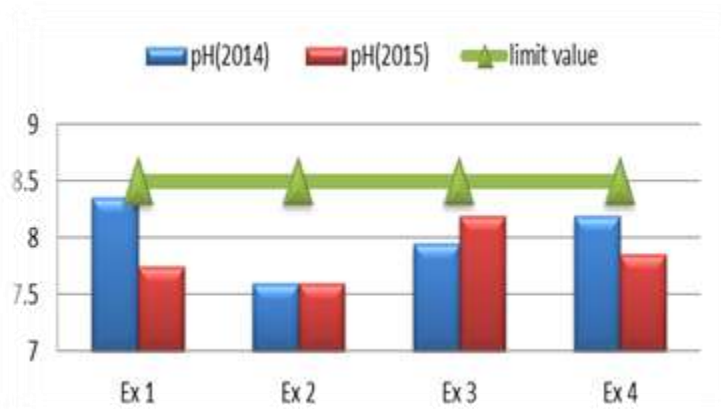


Figure 4. Evolution of the mine water discharges pH during the C1 and C2 campaigns.

The mine water discharges have a neutral to slightly alkaline pH ($7 < \text{pH} < 8.5$), which indicates an absence of the acid character of the mine water, which is the main character of acid mine drainage (AMD) [60], in all the samples analyzed in C1 and C2. The variation in the pH contents of the mine water discharges between C1 and C2 is linked to several factors, including the depth of the mine, because as the water circulates deeper in the mine, its overall mineralization increases due to the geochemical background changes resulting from the advancement of mining operations. As well as the residence time of mine water in the mine and the contact time of mine water with the rocks (leaching of the bottom walls) because when the transit time of this water is sufficient, it occurs exchange of bases between the cations of the clays from the bottom of the mine and the cations

contained in the water, which causes further changes in pH concentrations [61]. This seasonal variation in the mine water pH concentration can also be related to the rainfall conditions of the sampling period, because during a heavy rainy event the mine water records a supply of meteoric origin water. This water is very weakly mineralized with a rather acidic tendency (pH of rainwater between 6 and 6.5), which causes the drop of the mine water pH concentrations [62].

This neutral to basic character of the mine water can be explained by the fact that the AMD phenomenon is not encountered in all sulfide mineral mining operations, especially when mineral phases in the bedrock are able to neutralize the acidity produced [45,57]. With the presence of carbonate, the acidity produced is neutralized by the dissolution of carbonates which greatly slow the solubilization rate of contaminating metallic trace elements. It is a neutral mining drainage (NMD) [63]. The capacity of the sulfides to produce acid is determined by the relative content of the acid-generating mineral phases and the acid-consuming phases; if the acid-consuming such as calcite and bauxite are present, the resulting water can be neutral pH containing high concentrations of sulfate and metals [64]. In the geological context of the studied area, the presence of carbonate minerals such as calcite, promotes a natural neutralization in situ of the acidity of the mine water discharges by producing a NMD [65,66].

3.1.2. SULFATE

The sulfate contents vary during the C1 between 131 mg/L recorded at the station Ex 3, and 1413 mg/L recorded at the station Ex 4, and between 131 mg/L at the station Ex 1 and 1310 mg/L at the Ex 4 station during the C2 (Figure 5). The station Ex3 shows the two lowest sulfate concentrations noted in both C1 and C2 campaigns with a slight increase in C2. However, the station Ex 4 shows the two highest sulfate concentrations recorded during both C1 and C2 campaigns, with a significant decrease in C2.

All sulfate concentrations recorded at the mine water discharges during the C2 are lower than those recorded during the C1, except on the station Ex 3. The sulfate values recorded at the totality of the mine water discharges sampling stations exceed the limit value of the industrial discharges set at 500 mg/L, except on the station Ex 3, which represents lower concentration to the standards during the two analysis campaigns (Figure 5).

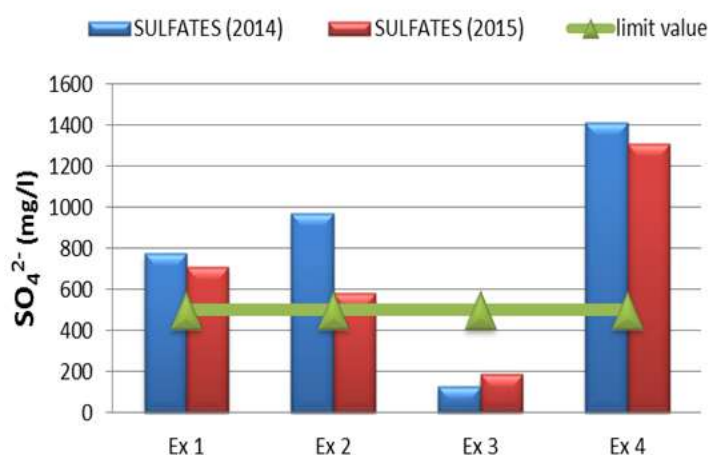


Figure 5. Evolution of sulfate content of the mine water discharges during the C1 and C2 campaigns.

The high concentration of sulfate in the mine water discharges is mainly related to the exploitation of sulfide ore [66] due to the oxidation of the mineral sulfides by producing heavy metals and sulfate [67].

The variation in the sulfate contents between C1 and C2 at the Ex1 and Ex2 stations is linked to the progress of the underground mining works, because the geochemical background changes and induces the modification of the mineralization of the mine water discharges. The increase of the depth of the exploited levels induces the decrease of the sulfate contents because the high sulfate contents characterize the water circulating through shallow mining works [61,68–70]. The factor of the contact time of the mine water discharges with sulfide rocks at the mine (residence time in the mine) can also be a determining factor for the sulfate concentrations in the mine water discharges, because sulfates come from the oxidation of pyrites at the contact of water and air [61,71].

Furthermore, the sulfate concentration recorded in the station Ex 3, which does not exceed the industrial waste limit values during the C1 and C2 analysis campaigns, is probably related to the dilution phenomenon, since the final discharges sampled in this station are composed of the mixture of mine water used for mining and a large part of the dewatering of the deposit which has a significant water wealth. The discharges rate at this station accounts for more than the half of the mine's water discharges.

3.1.3. ALUMINUM

Aluminum concentrations show a very low variation during the C2. However, during the C1, the values recorded at the four measurement stations are less than 1.5 mg/L, except on the station Ex 2, which has a value of 14.1 mg/L, which exceed the limit value of the industrial discharges in the surface and underground waters setting the threshold value at 10 mg/L (Figure 6).

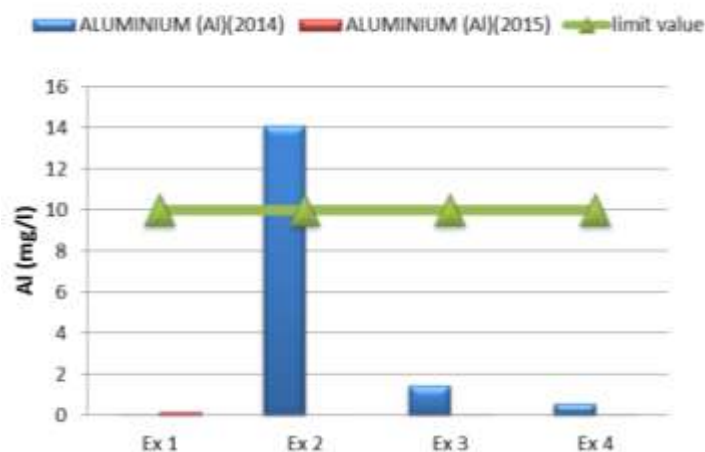


Figure 6. Evolution of the aluminum content of the mine water discharges during the C1 and C2 campaigns.

Aluminum is the second most abundant metal in the earth after iron [72]. The origin of aluminum in the mine water discharges can be linked to the geochemical alteration of rocks in contact with water and oxygen during mining it corresponds to total hydrolysis, which results in the release and drainage-driven elimination of minerals constituents. It should be noted that iron and aluminum oxyhydroxides are insolubilized. This alteration leads to the formation of newly formed

clays, which can induce an increase in the turbidity of the mine water discharges circulating through the mine. Thus, the turbidity of the mine water discharges can be a determining factor of the high aluminum content recorded at point Ex2 during C1, because the increase of the turbidity induces an increase of the aluminum concentration in the mine water [73]. The high aluminum content at point Ex2 during C1 can also be linked to the pH of the mine waters, because the solubility of aluminum is low in waters with a pH close to neutrality between 7 and 7,5, while the precipitation of aluminum requires a pH greater than 5 [73,74].

Also, the aluminum can be related to the natural erosion phenomena of the mountain, because it comes mainly from the mechanical training of alumino-siliceous minerals, which are easily mobilized, present in amorphous gels (allophanes type) and / or watershed clays [75].

3.1.4. IRON

The iron concentrations recorded at the mine water discharges during the C2 are lower than those recorded during the C1, except at the station Ex 1 (Figure 7). Like aluminum, the iron concentrations recorded during the C1 and C2 analysis campaigns are below the limit recommended by the limit values of industrial discharges in surface or underground waters fixed at 5 mg/L, except at the station Ex 2, which represents a value of 25.5 mg/L during the C1, far exceeding the limit value.

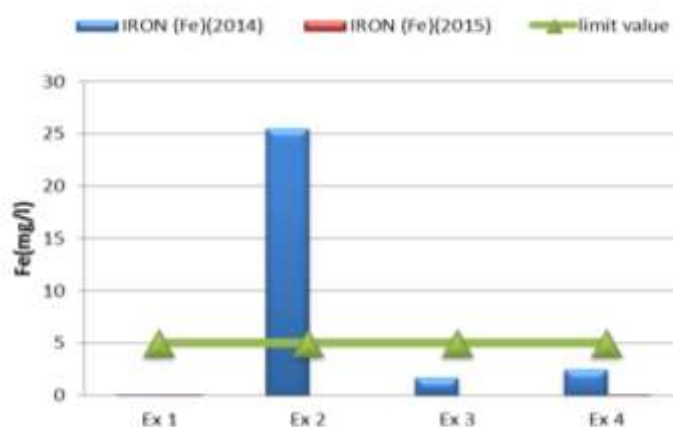


Figure 7. Evolution of the iron content of the mine water discharges during the C1 and C2 campaigns.

During the mining of a massive rock containing sulfide minerals, the pumping of the mine's dewatering in the surrounding lands an area that was previously saturated, which put the sulfide minerals in contact with the oxygen and the water of percolation. This induces the alteration of all readily oxidizable minerals, through the formation of sulfates and hydroxides, carbonates and other oxygenates characteristic of what is called the oxidation zone of mineral deposits. The Pyrite, which is the most widespread sulfide in the earth's crust, oxidizes to ferrous sulfate which, in the presence of free oxygen, is transformed into ferric sulfate [75]. This could explain the high concentration of Iron at the station Ex 2 because the deposit 2 is rich in pyrite [19,57,65,66,76].

3.1.5. MANGANESE

The Manganese concentration recorded values indicate an irregular contamination. Indeed, they vary, at the 4 stations, between a minimum value of 0.003 mg/L recorded in the station Ex 3 during the C2 and a maximum value of 8.78 mg/L noted in the station Ex 2 during the C1, thus exceeding the limit value fixed at 1 mg/L. Seasonal variability is recorded at the station Ex 1, which has a concentration of 0.075 mg/L during the C1 and a concentration of 7.35 mg/L during the C2 (Figure 8).

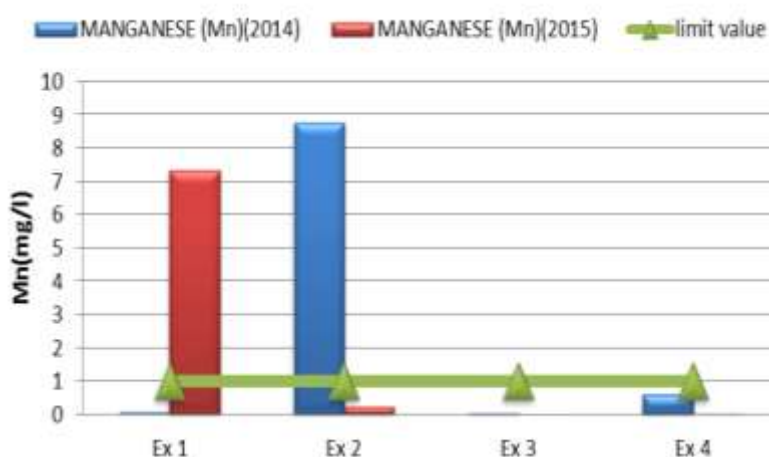


Figure 8. Evolution of the Manganese content of the mine water discharges during the C1 and C2 campaigns.

Like iron and aluminum, the high concentration of Manganese at the station Ex 2 during the C1 and at the station Ex 1 during the C2 can be related to the oxidation of pyrite [19,57,76], following the percolation of the mine's water through the mining cavities of sulfide lands [75].

The remarkable decrease in the concentration of aluminum, iron and manganese at the station Ex 2, between the C1 and C2 campaigns is due to the change of the geochemical background, this is being the case because when the depth of the mine increases the water circulates deeper in the mine, and its overall mineralization changes [61,70].

3.1.6. ARSENIC

The arsenic values recorded at the totality of the mine water discharges sampling stations do not exceed the limit values of industrial discharges in surface or underground waters set at 50 $\mu\text{g/l}$, except in the Ex 2 station which had a concentration above the standard during the C1. During the C1, they show significant variability from downstream to upstream of the mine, which varies between 83 $\mu\text{g/l}$ and 2.5 $\mu\text{g/l}$ at the Ex 2 and the Ex 1 stations respectively (Figure 9).

However during the C2, the variation of the arsenic contents is less important with values much lower than those recorded in the C1, and which vary between 25 $\mu\text{g/l}$ at the station Ex 3 and 3,6 $\mu\text{g/l}$ at the Ex 1 and Ex 4 stations.

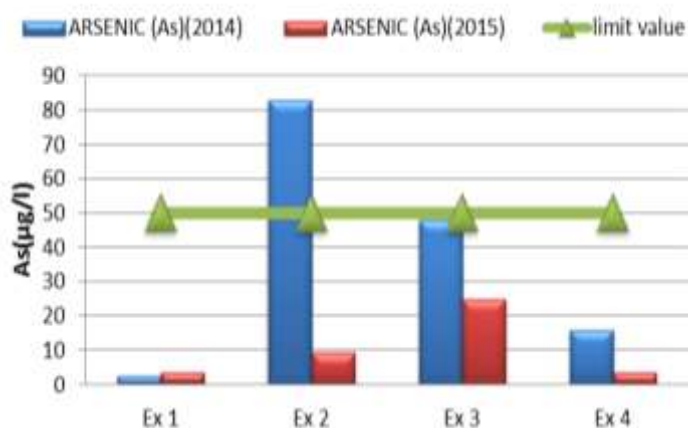


Figure 9. Evolution of the Arsenic content of the mine water discharges during the C1 and C2 campaigns.

The arsenic ultimate source in the mine waste is the primary arsenopyrite in the ore concentrates. Arsenic is commonly associated with metallic mineral deposits. While arsenic is naturally mobilized from these deposits, mining and beneficiation of the deposits can significantly amplify arsenic mobilization. Once the ore has been excavated, processed, and discarded in waste rock piles and tailing, percolating rainwater can facilitate oxidation and dissolution of arsenic from the mine wastes and mine excavations. Dissolved arsenic can then be discharged into the environment with potentially toxic consequences for the downstream biota. Mining and tailings disposal promotes oxidative arsenic mobilization by increasing permeability and increasing contact between arsenic sulfides and oxygenated water. Hence, anthropogenic interference accelerates the natural processes of arsenic mobilization and dispersal into streams.

Arsenic is initially present in sulfide compounds such as arsenopyrite (FeAsS), orpiment (As_2S_3) or realgar (AsS) [77–81]. The arsenic contents in the waters vary according to the lithology crossed, the climate and the anthropic contribution [79]. And since it comes in different chemical forms (like many other elements), its speciation depends on the pH and the redox potential [82,83].

The visible decrease in the concentration of arsenic at point Ex 2 during C2, is probably linked to the decrease in the concentrations of Fe, Al and Mn in the mine water discharges of this point, because the oxyhydroxides of these elements constitute alongside clays and organic matter a significant fraction of the arsenic trapping during the weathering which plays an important role in controlling the concentration of dissolved arsenic [84–89].

3.1.7. LEAD, CADMIUM, COPPER, AND ZINC

The levels of lead, cadmium, copper and zinc recorded at the totality of the mine water discharges sampling stations, have a small spatial and temporal variability (Figure 10). They remain very low and do not exceed the limit values for industrial discharges set at $1000 \mu\text{g} / \text{l}$ for lead, $200 \mu\text{g} / \text{l}$ for cadmium, $3000 \mu\text{g} / \text{l}$ for copper and $5000 \mu\text{g} / \text{l}$ for zinc.

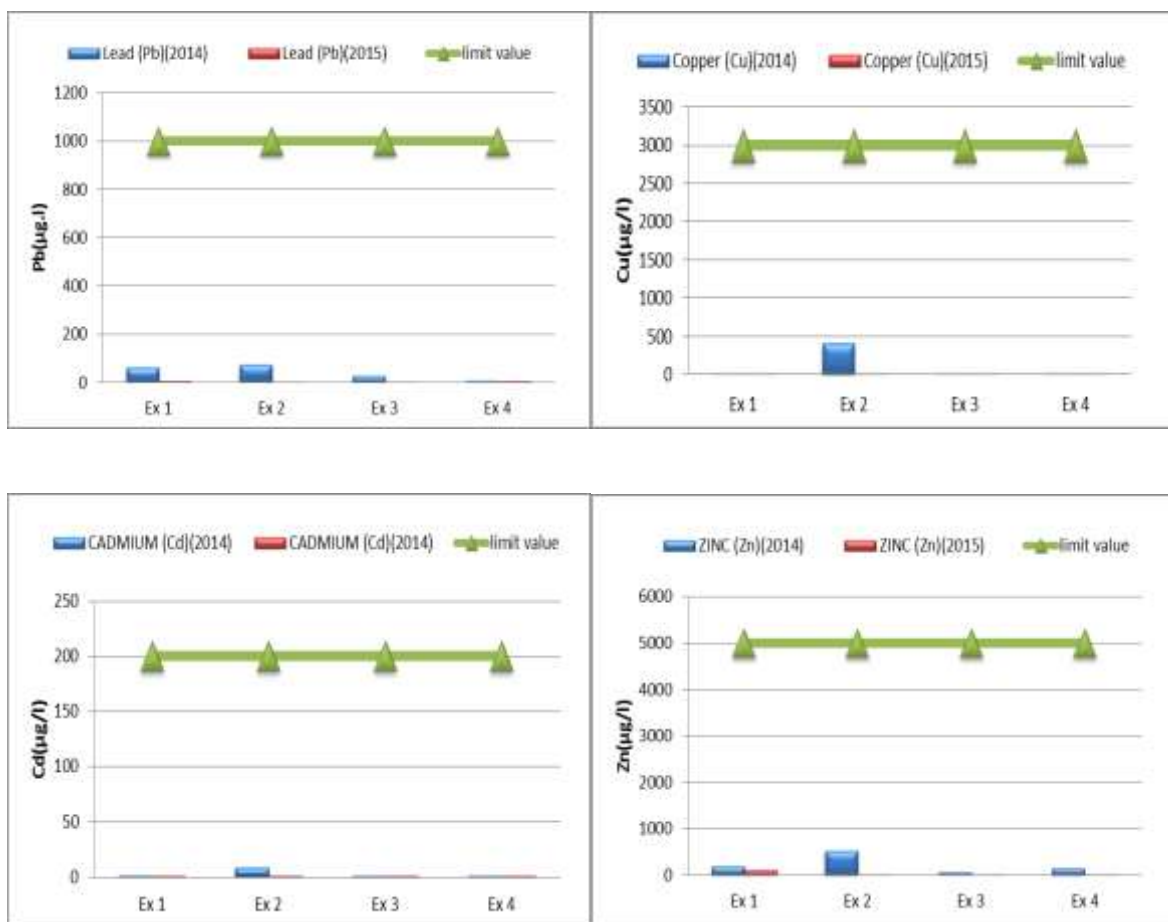


Figure 10. Evolution of lead, cadmium, copper and zinc contents of water discharges during the C1 and C2 campaigns.

In waters, lead (Pb) has a strong affinity for sedimentary particles including clays, oxy-hydroxides of iron and manganese, sulfides and organic matter [90]. It can also be associated with carbonates when the medium is poor in organic matter and in oxy-hydroxides of Fe or Mn [91]. While zinc (Zn) is in ionic form, it is complexed by organic ligands (fulvic and humic acids) or even associated with inorganic colloids. In waters with pH below 8, the concentrations of zinc in the cationic form (Zn^{2+}) are greater, while the neutral species ZnCO_3 is predominant in waters with pH above 8 [92]. Furthermore, the zinc is complexed with sulfates in waters with an acid pH and can precipitate in the form of sulfated salts under extreme acid conditions [93,94]. For the Cadmium (Cd) in waters and pH value below 8, it is present in the dissolved state as Cd^{2+} form, preferentially complexed by humic substances [95]. And in an anoxic environment, it precipitates with S^{2-} even at very low concentrations [24].

In waters the copper (Cu) is mainly found in divalent form Cu (II), while the monovalent form Cu (I) is present only at extremely low concentrations since it reacts to form metallic copper and Cu (II) ions. Cu (I) can be produced under reducing conditions and the majority of the compounds formed are insoluble [96,97].

The Copper in complexed form is associated with inorganic and organic ligands. This complexation of Cu by organic ligands strongly conditions its bioavailability, because the organically complexed copper is very stable [98]. The metallic cations (Pb, Zn, Cu and Cd) generally show low

concentrations in the waters of mining lakes when the pH is alkaline [99]. This is the case of the HBM mine water discharges, which is located in limestone soils [38,55] where acidic waters are quickly neutralized by carbonates, and where most metals become insoluble and precipitate [100].

3.2. National studies

In Morocco, currently there are active mines producing a variety of mineralization processes, and there have been many closed and abandoned mines since the 1970s. Recently, some studies have been interested in the environmental impact of abandoned mines and sites as well as the recovery of their waste. Let us cite those of [101] and [102], on the Kettara mine and [103] on the Sidi Bou Othmane mine in the Jebilet; we can also refer to those carried out in Haute-Moulouya [104–107]., in central Morocco on the Tighza mine [108], on the Mohammedia salt mine [109] and on the Jerrada mine [110]. The studies on zones near the mining centers of Aouli and Mibladan in Haut Moulouya have shown a negative impact of mining activities, especially the contamination of surface water, sediments, soil and plants [63,106,111,112], as well as pollution by heavy metals of surface water of Moulouya river [100,113].

The evaluation of the physico-chemical quality and the MTE load of the mine water discharges is an inseparable part of the evaluation of the impact of mining on the environment, because it can be indicative of the origin of any metal detected in excess in surface water, groundwater or sediments surrounding mines. However in most of the environmental impact studies the mine water discharges are considered as natural waters discharges from the mine, however the drainage of this water through the mine cavities can induce their load in MTE., which can have an impact on the environment once this mine water is discharged or infiltrated into the underground water.

Table 2. Comparative table of the average concentrations of metallic trace elements in the HBM water discharges and in the mine water discharges of other mines in Morocco.

	Average MTE concentrations (µg/L)					Industrial site	Study area	Exploited substance	Reference
	Pb	Cd	As	Cu	Zn				
Mine water discharges	23, 17	1, 4	23, 87	53, 81	131, 67	HBM	Sebou watershed	n. d	This Work
Mine lakes	27, 5	n. d	92,825	n. d	n. d	Zeïda Mine	Haute Moulouya	Pb	[111]
drainage water	n. d	n. d	n. d	58000	45000	Kettara Mine	Kettara River Jebilet	Fe-S	[102,116,117]
Mine lakes	31, 186	n. d	111, 202	n. d	n. d	Zeïda Mine	Haute Moulouya	Pb	[63]
Leachate of mine tailing	306, 875	9, 125	763	100686	8597	Kettara Mine	Kettara River Jebilet	Fe-S	[115]

n. d.: Undetermined value

In Morocco, in the majority of the impact of mining on the environment evaluation studies, the physico-chemical characterization and the evaluation of the contamination in MTE are focused on the evaluation of the water quality and sediments surrounding mining sites. In such studies, the designation of mine discharges is attributed to all liquid or solid mine discharges (spoil tip; dumps; *AIMS Environmental Science* Volume 8, Issue 1, 60–85.

ore processing residues; water from quarry lakes and infiltration at the foot of the tailings dam). As an example of the studies characterizing the quality of solid discharges from the mine or the ore processing plant, we can cite the work on the Tourtit and Ichoumellal mines [2], the Zeïda, Mibladen and Aouli mines [106,113], the Sidi Bou Othmane mine [103], the Kettara mine [101,102,114,115].

Since we are interested in the HBM mine water discharges, in our study the concentrations of metallic trace elements evaluated in this study were compared with some national studies (Table 2), which are concerned with the evaluation of metallic trace elements in mining areas and their concentrations in mine liquid discharges [63,102,111,115–117]:

The origin of the waters and their course define their hydro-chemical character and, hence the difference in MTE contents in mine liquid discharges compared to the levels in the HBM mine water discharges.

In the case of the Zeïda mine, water is sampled at the level of the mining lakes, which is located at the foot of the spoil tip and the tailings dam. The arsenic and lead concentrations are higher than the levels recorded in HBM's mine water discharges. These discharges have a common character with the waters of the mining lakes of Zeïda which is the neutral pH to slightly alkaline influencing the solubility of the MTE due to the fact that the metallic trace element (Pb, Zn, Cd, Cu, ...) show high concentrations in acid mining lakes, while the MTE (As and Se) are generally at high concentrations in alkaline mining lakes [63,99].

For the drainage water from the kettara mine, samples were taken from various pits collecting runoff water of the tailings pond and runoff water of the waste rock [102,116,117]. These drainage waters have much higher copper and zinc contents than those recorded in the HBM mine water.

The leachate of the kettara mine tailings are obtained by mixing 150 g of tailings with 300 ml of distilled water (Ratio 1/2), with permanent agitation, and after a week, the filtration was carried out, then the measurements of the concentrations of MTE in the leachate water, these analyses show that the As and Pb contents are higher at the top of the pile of mining residues, which can be explained by the acidic pH on the surface of the pile of mining residues in direct contact with the oxygen. The values recorded in As, Pb, Cu, Cd and Zn at the leachate of the tailings of the kettara mine are much higher than those recorded at the HBM's water discharges.

The MTE concentrations in the HBM water discharges are the lowest compared to other liquid discharges from other mines, something which can be linked to several factors, including: the geochemical background of the mine, the waters contact time with the rocks, the nature of the residues that the water percolates through and finally the pH of the water which plays an important role in the degree of passage of the MTE in the aqueous phase.

3.3. *International studies*

The concentrations of metallic trace elements evaluated in this study were compared with some international studies (Table 3), which are concerned with the evaluation of metallic trace elements in mining areas and their concentrations in mine water discharges [118–120].

The average concentration of lead (Pb) recorded in the HBM water discharges is lower than the one noted in the mine water discharges of the abandoned Escarro mine in France, which was exploited between 1960 and 1991, according to the environmental impact study of the Escarro's mine developed in 1983 [118]. In terms of lead, the average concentration in the HBM mine's water is in second class after that of the Escarro mine, then in third class that of the Malines mine in France, and

in the last class that of the Soughs mine in England.

Table 3. Comparative table of the average concentrations of metallic trace elements in the HBM water discharges and in the mine water of four other active and abandoned mines worldwide.

		Average MTE concentrations ($\mu\text{g/L}$)					Industrial site	Study area	Exploited substance	Reference
		Pb	Cd	As	Cu	Zn				
Morocco	Ex1 (C1)	61	1,1	2,5	4,2	190	HBM	Sebou watershed	n.d	This work
	Ex1 (C2)	5, 6	0, 5	3,6	2	115				
	Ex2 (C1)	72	8, 3	83	406	528				
	Ex2 (C2)	1, 7	0, 2	9,3	1, 4	2, 2				
	Ex3 (C1)	28	0, 3	48	3, 3	60				
	Ex3 (C2)	1, 7	0, 2	25	1, 4	2, 2				
	Ex4 (C1)	9	0, 4	16	8, 8	143				
	Ex4 (C2)	6, 4	0, 2	3, 6	3, 4	13				
	Average	23, 17	1, 4	23, 87	53, 81	131, 67				
France		29	n. d.	2, 14	5	9, 28	Escarro mine	Languedoc Roussillon Têt watershed	CaF ₂	[119]
		11, 12	2, 7	n. d.	n. d.	4,21	Malines mine	Saint-Laurent-le-Minier Hérault watershed	Pb, ZnS, PbS, Zn	[118]
		10, 2	0, 84	n. d.	0, 56	160, 2	Soughs mine	Derbyshire Bugsworth watershed	Pb	[118]
Norway		n. d.	12800	280	574000	5640000	Killingdal mine	Sør-Trøndelag Gaula watershed	Cu Zn S	[120]

n. d.: Undetermined value

For the Cadmium (Cd), the average concentration recorded in the mine water discharges of the HBM is in third class after that of the Killingdal mine in Norway, and that of the Malines mine in France, and in the last class that of the Soughs mine in England. In terms of Arsenic (As), the average concentration in the HBM water discharges is in second class after that of the Killingdal mine in Norway, and in the last class that of the Escarro mine in France.

The average concentration of copper (Cu) in the HBM water discharges is in second class after that of the Killingdal mine in Norway, then in third class that of the Escarro mine in France, then in the last class that of the Soughs mine in England. And for the Zinc (Zn), the average concentration recorded in the HBM water discharges is in third class after that of the Killingdal mine in Norway, and that of the Soughs mine in England. In fourth class that of the Escarro mine in France then that of the Malines mine in France.

It should be noted that the physicochemical characterizations of mine waters compared to the HBM are developed as part of studies aimed at the sustainable management of mine water discharges and the reduction of their environmental impacts. For the rest of the mines, it is in the context of an environmental impact study for the continuation of exploitation for the Escarro mine, and in the context of the performance monitoring of the treatment station of mine water discharges for the Malines mine, and post-mine monitoring and impact assessment for the Soughs and the Killingdal mines. The differences among the average concentrations of MTE contained in the mines waters

show the importance of the lithology of the host rock, rather than the mineralogy of the ore, for the quality of the mine water [120].

The oxidation of sulfide minerals to release heavy metals, sulfate and acid is the fundamental reaction characterizing acid mine drainage [60,121–123]. However, the quality of mines waters can be adversely affected by other parameters such as the kinetic factor because of the relatively slow rate of dissolution and oxidation of sulfide minerals compared to the rapid flux of limestone groundwater through the mine conduits [38,55]. And the solubility of heavy metals that is suppressed by the high alkalinity of water, as well as other parameters that may negatively influence the global quality of mine water discharges such as the salinity, the traces of explosives based on nitrogen oxidized to nitrates and the organic parameters [120].

The mine water discharges of the HBM are classified as one of the least charged mine water in terms of MTE compared to other mines (Table 3).

3.4. *Synthesis*

The physicochemical characterization of the mine water and the evaluation of their load in metallic trace elements (MTE) showed a small variability in time and space between the four stations sampled, and absenteeism of the acidic nature of mine's water. The majority of the analyzed mine waters presents important concentrations of sulfate. During the C1 at the point Ex2 theirs is contamination of Iron, Aluminum, Manganese and Arsenic. However, the concentrations of Pb, Cd, Zn and Cu elements remain conform and very low compared to the limit of standards.

The monitoring of the overtake elements made it possible to identify the degree of contamination of the mine's water discharges, and to note an improvement in time in the mine water discharges quality. This variation in element concentrations between the C1 and C2 campaigns is due to the change of the geochemical background, because with the progress of the mining operations, the geochemical background changes, influencing the hydro-chemical composition of the percolated mine water through the walls of the mine before its rise to the surface of the ground, forming the final discharges.

The mine water discharges of the HBM are classified as one of the least charged mine water in terms of MTE concentration compared to other national liquid mine discharges and to other mine waters worldwide.

4. **Conclusion**

The evaluation of the quality of the discharges of mine water elaborated in this study for the first time, to our knowledge, at the level of the beht basin, sub-basin of Sebou, allowed to identify the quality of the discharges of mine water and their load in MTE in order to evaluate the impact of these discharges on the environment. Thus the evaluation of the mining contribution in the modification of the quality of the environment surrounding the Haut beht mine.

The mine water remains a reservoir of contamination able to drop in the aqueous phase other elements by the phenomenon of leaching and dredging in the wet phase. Therefore it presents a potential toxicological risk in the absence of specific means of sustainable management aimed at safeguarding the surrounding environment of the mine and mitigating the potential impact of the mine water discharges into the environment.

Despite the absence of contamination of the HBM water discharges, their pH-dependent nature draws attention to the possibility of an MTE loading of the sediments and the waters surrounding the mine. The potential impacts of the mine's water discharges on the quality of groundwater, surface water, and sediments will be the subject of other ongoing works.

The diagnosis elaborated through the analysis and the quantification of the different parameters and their impacts, allowed to draw up a first report on the variability of the mine's waters discharges quality and their potential impacts on the environment.

Thus, the monitoring of environmental indicators may be essential for all industrial activity to limit their potential impacts on the environment.

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Conflict of interest

The authors declares that there is no conflict of interests regarding the publication of this paper.

References

1. Ghoreychi M, Laouafa F, Poulard F. L'après-mine et la mécanique des roches; 2017.
2. Ahmedat C, El hassani I-EEA, Zarhraoui M, et al. (2018) Potentialités minérales et effet de géo-accumulation des éléments traces métalliques des rejets des mines abandonnées. L'exemple des mines d'antimoine de Tourtit et d'Ichoumellal (Maroc central). *Bull Inst Sci Rabat* 71–89.
3. Brodtkom F (2001) Good Environmental Practice in the European Extractive Industry: A Reference Guide, with Examples from the Industrial Minerals and Gypsum Industries: IMA-Europe.
4. Chakraborty P, Gopalapillai Y, Murimboh J, et al. (2006) Kinetic speciation of nickel in mining and municipal effluents. *Anal Bioanal Chem* 386: 1803–1813.
5. McClure R, Schneider A (2001) The General Mining Act of 1872 has left a legacy of riches and ruin. *Seattle Post-Intelligencer* 11.
6. Plumlee GS (1999) The environmental geology of mineral deposits. *The environmental geochemistry of mineral deposits Society of Economic Geologists Part A*: 71–116.
7. Touzara S, Amlil A, Ennachete M, et al. (2020) Development of Carbon Paste Electrode/EDTA/Polymer Sensor for Heavy Metals Detection. *Anal Bioanal Electrochem* 12: 644–652.
8. Salvarredy Aranguren MM (2008) Contamination en métaux lourds des eaux de surface et des sédiments du Val de Milluni (Andes Boliviennes) par des déchets miniers. Approches géochimique, minéralogique et hydrochimique: Université de Toulouse, Université Toulouse III-Paul Sabatier.
9. Armiento G, Nardi E, Lucci F, et al. (2017) Antimony and arsenic distribution in a catchment affected by past mining activities: influence of extreme weather events. *Rendiconti Lincei* 28: 303–315.

10. Benvenuti M, Mascaro I, Corsini F, et al. (1997) Mine waste dumps and heavy metal pollution in abandoned mining district of Boccheggiano (Southern Tuscany, Italy). *Environ Geol* 30: 238–243.
11. Galán E, Gómez-Ariza J, González I, et al. (2003) Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. *Appl. Geochem. Appl Geochem* 18: 409–421.
12. González RC, González-Chávez M (2006) Metal accumulation in wild plants surrounding mining wastes. *Environ Pollut* 144: 84–92.
13. Hilton J, Davison W, Ochsenein U (1985) A mathematical model for analysis of sediment core data: Implications for enrichment factor calculations and trace-metal transport mechanisms. *Chem Geol* 48: 281–291.
14. Jian-Min Z, Zhi D, Mei-Fang C, et al. (2007) Soil heavy metal pollution around the Dabaoshan mine, Guangdong province, China. *Pedosphere* 17: 588–594.
15. Luoma SN, Rainbow PS (2008) Metal contamination in aquatic environments: science and lateral management: Cambridge university press.
16. Mlayah A, Da Silva EF, Rocha F, et al. (2009) The Oued Mellègue: Mining activity, stream sediments and dispersion of base metals in natural environments, North-western Tunisia. *J Geochem Explor* 102: 27–36.
17. Tessier E (2012) Diagnostic de la contamination sédimentaire par les métaux/métalloïdes dans la Rade de Toulon et mécanismes contrôlant leur mobilité
18. Azzaoui s, El hanbali m, Leblanc m (2002) Note technique/Technical Note Cuivre, plomb, fer et manganèse dans le bassin versant du Sebou; Sources d'apport et impact sur la qualité des eaux de surface Copper, Lead, Iron and Manganese in the Sebou. *Water qual Res J* 37: 773–784.
19. Benaabidate L (2000) Caractérisation du bassin versant de Sebou: Hydrologie, Qualité des eaux et géochimie des sources thermales. *Docteur Essciences, Univ S MBA, Fès (Maroc)* 228.
20. Foudeil S, BOUNOUIRA H., EMBARCH K., et al. (2013) Evaluation de la pollution en métaux lourds dans l'oued sebou (Maroc).
21. Foutlane A, Saadallah M, Echihabi L, et al. (2002) Pollution by wastewater for olive oil mills and drinking-water production. Case study of River Sebou in Morocco.
22. Derwich E, Benaabidate L, Zian A, et al. (2010) Caractérisation physico-chimique des eaux de la nappe alluviale du haut Sebou en aval de sa confluence avec oued Fès. *LARHYSS J ISSN* 1112–3680.
23. Derwich E, Beziane Z, Benaabidate L, et al. (2008) Evaluation de la qualité des eaux de surface des Oueds Fès et Sebou utilisés en agriculture maraîchère au Maroc. *LARHYSS J ISSN* 1112–3680.
24. Hayzoun H (2014) Caractérisation et quantification de la charge polluante anthropique et industrielle dans le bassin du Sebou.
25. Lakhili F, Benabdelhadi M, Bouderkha N, et al. (2015) Etude de la qualité physico-chimique et de la contamination métallique des eaux de surface du bassin versant de Beht (Maroc). *Eur Sci J ESJ* 11.
26. Qaouiyyid A, Hmima H, Hourri K, et al. (2016) Les Teneurs Métalliques Et Paramètres Physico-Chimiques De L'eau Et Du Sédiment De Oued Beht, Au Niveau De Sidi Kacem Et De Oued R'dom Au Niveau De Sidi Slimane. *Eur Sci J ESJ* 12.

27. Essamt F (2016) Etude de la qualité d'eau de oued beht dans la région de Sidi Slimane.
28. Lamhasni N, Chillasse L, Timallouka M (2017) Bio-Évaluation De La Qualité Des Eaux De Surface D'oued Beht (Maroc) Indice Biologique Global Des Réseaux De Contrôle Et De Surveillance (IBG-RCS).
29. Abdallaoui A (1998) Contribution à l'étude du phosphore et des métaux lourds contenus dans les sédiments et de leur influence sur les phénomènes d'eutrophisation et de la pollution: Cas du bassin versant de l'Oued Beht et de la retenue de barrage El Kansera.
30. Bouchouata O, Ouadarrri H, El Abidi A, et al. (2012) Bioaccumulation des métaux lourds par les cultures maraîchères au niveau du Bassin de Sebou (Maroc). *Bull Inst Sci Rabat* 34: 189–203.
31. Kenfaoui A (2008) Economisons l'eau en la préservant de la pollution. *REV HTE*: 140–117.
32. Michard A, Soulaïmani A, Hoepffner C, et al. (2010) The south-western branch of the Variscan Belt: evidence from Morocco. *Tectonophysics* 492: 1–24.
33. Piqué A, Michard A (1981) Les zones structurales du Maroc hercynien. *Geol Sci Bull Papr* 34: 135–146.
34. Ouabid M, Ouali H, Garrido CJ, et al. (2017) Neoproterozoic granitoids in the basement of the Moroccan Central Meseta: correlation with the Anti-Atlas at the NW paleo-margin of Gondwana. *Precambrian Res* 299: 34–57.
35. Tahiri A, Montero P, El Hadi H, et al. (2010) Geochronological data on the Rabat–Tiflet granitoids: their bearing on the tectonics of the Moroccan Variscides. *J Afr Earth Sci* 57: 1–13.
36. El Hadi H, Tahiri A, El Maidani A, et al. (2014) Geodynamic setting context of the Permian and Triassic volcanism in the northwestern Moroccan Meseta from petrographical and geochemical data.
37. Ben Abbou M (1990) Evolution stratigraphique et structurale, au cours du Paléozoïque, de la bordure nord du Massif central (région d'Agourai, Maroc). *Unpubl Thesis Univ Fès*.
38. Izart A, Tahiri A, El Boursoumi A, et al. (2001) Carte géologique du Maroc au 1/50 000, feuille de Bouqachmir. *Notes et mémoires Serv géol Maroc*.
39. Cailleux Y (1974) Géologie de la région des Smaala (Massif central marocain): stratigraphie du primaire, tectonique hercynienne.
40. Tahiri A (1994) Tectonique hercynienne de l'anticlinorium de Khouribga-Oulmès et du synclinorium de Fourhal. *Bull Inst Sci Rabat* 18: 125–144.
41. Tahiri A, Hoepffner C (1987) La faille d'Oulmès (Maroc central hercynien): cisaillement ductile et tectonique tangentielle. *Bull Inst Sci Rabat* 11: 59–68.
42. Sebbag I (1970) Etude géologique et métallogénique de la région du Tafoudeit. *Rapport du Service Régional de Géologie-Meknès, service d'étude des gîtes minéraux* 29: 62p.
43. Rassou KK, Razoki B, Yazidi M, et al. (2019) The vulgarization for the patrimonialization of the kettara geodiversity (central jbilel) morocco.
44. Nerci K (2006) Les minéralisations aurifères du district polymétallique de Tighza (Maroc central): un exemple de mise en place pégrinitique tardi-hercynienne.
45. Giuliani G (1984) Les concentrations filoniennes à tungstène-étain du massif granitique des Zaër (Maroc Central): minéralisations et phases fluides associées. *Mineralium Deposita* 19: 193–201.

46. Salama L, Mouguina EM, Nahid A, et al. (2016) Apport de la modélisation géologique 3D à l'exploration minière: Etude de cas du gisement de Draa Sfar (Jbilettes centrales, Maroc) [Mining exploration using 3D geological modeling: Draa Sfar deposit's case study (Central Jbilettes, Morocco)].
47. Marcoux E, Belkadir A, Gibson HL, et al. (2008) Draa Sfar, Morocco: A Visean (331 Ma) pyrrhotite-rich, polymetallic volcanogenic massive sulphide deposit in a Hercynian sediment-dominant terrane. *Ore Geol Rev* 33: 307–328.
48. Rziki S (2012) Environnement géologique et modèle 3D du gisement polymétallique de Draa Sfar (Massif hercynien des Jbilettes, Maroc): Implications et perspectives de développement: Thèse de Doctorat Présentée à la Faculté des Sciences Semlalia Marrakech
49. DEM Dddm (2011) Les principales mines du maroc. In: Ministère de l'énergie dm, de l'eau et de l'environnement direction du développement minier, editor. Éditions du service géologique du maroc Rabat ed.
50. Onhym Ondhedm (2020) Oulmes (sn-w) (massif hercynien central, maroc).
51. Mint chevie M (2010) Contribution à l'étude hydroclimatique du bassin versant de l'Oued Beht, Maroc septentrional. Fès, Maroc: Université Sidi Mohammed Ben Abdellah Faculté des Sciences et Techniques. 58 p.
52. Burger J, Dardel R, Dutrieux E, et al. (1951) Carte géologique régulière du Maroc au 1: 100.000ème: Meknès nord, Feuille levée et éditée par la Société Chérifienne des Pétroles. *Notes et mémoires du Service*.
53. Laabidi A, Gourari L, El hamaidi A (2014) Typologie morpho-sédimentaire des dépôts actuels de la vallée du Moyen Beht (Sillon sud rifain occidental, Maroc). *IOSR J Eng(IOSRJEN)* 4.
54. ABHS AdBHdS (2013) Étude d'actualisation du plan directeur d'aménagement intégré des ressources en eau de bassin hydraulique de Sebou. *Note de synthèse, Agence du bassin hydraulique du Sebou*.
55. Duchaufour P (1977) Pédologie: Tome 1: Pédogénèse et classification: Masson.
56. Bryssine G (1966) Etude des propriétés physiques des dess de l'oued beht. *Al Awamia* 2: 85–123.
57. Rachdi HE-N (1995) Etude du volcanisme plio-quadernaire du Maroc central: pétrographie, géochimie et minéralogie: comparaison avec des laves types du Moyen Atlas et du Rekkam (Maroc): Editions du Service géologique du Maroc.
58. Schmiermund R, Drozd M (1997) Acid mine drainage and other mining-influenced waters (MIW). *Mining Environmental Handbook: Effects of Mining on the Environment and American Environmental Controls on Mining*: World Scientific. 599–617.
59. Karim A (2007) Le système siliciclastique-carbonaté de la marge sud-ouest paléotéthysienne au viséen supérieur: enregistrements paléoenvironnementaux et évolution dans un bassin d'avant pays (Tizra: Maroc central): Paris 11.
60. Pabst T (2011) Etude expérimentale et numérique du comportement hydro-géochimique de recouvrements placés sur des résidus sulfureux partiellement oxydés: Ecole Polytechnique, Montreal (Canada).
61. Blachere A (1985) Evaluation des impacts hydrogéologiques de l'arrêt d'une exhaure minière (vallées de l'Ondaine et du Lizeron, bassin houiller de la Loire): modélisation mathématique du milieu.

62. Armines ELEJ-MS (2010) Etat hydrog ochimique et  volution pr visionnelle du site des anciennes exploitations d'uranium de Lod ve (H rault). Centre de G osciences,  cole des mines de Paris, Fontainebleau, France
63. El Hachimi ML, EL Hanbali M, Fekhaoui M, et al. (2005) Impact d'un site minier abandonn  sur l'environnement: cas de la mine de Ze  da (Haute Moulouya, Maroc). *Bull Inst Sci Rabat* 93–100.
64. Bowell R, Bruce I (1995) Geochemistry of iron ochres and mine waters from Levant Mine, Cornwall. *Appl Geochem* 10: 237–250.
65. Piqu  A, Knidiri M (1994) G ologie du Maroc: les domaines r gionaux et leur  volution structurale: Pumag.
66. Taltasse P (1953) Recherches g ologiques et hydrog ologiques dans le bassin lacustre de F s-Mekn s: par P. Taltasse: F. Moncho.
67. Repeta DJ, Quan TM, Aluwihare LI, et al. (2002) Chemical characterization of high molecular weight dissolved organic matter in fresh and marine waters. *Geochim. Cosmochim. Acta.* 66: 955–962.
68. Debaisieux B (1983) G ologie appliqu e   l'am nagement urbain-Saint Etienne(Loire).
69. Hackbarth DA (1979) The effects of surface mining of coal on water quality near Grande Cache, Alberta. *Can J Earth Sci* 16: 1242–1253.
70. Barbier J, Chery L (1997) Relation entre fond g ochimique naturel et teneurs  lev es en m taux lourds dans les eaux (antimoine, arsenic, baryum, chrome, nickel, plomb, zinc). *Rapport BRGM* 39544: 51.
71. Herv  D (1980) Etude de l'acquisition d'une teneur en sulfates par les eaux stock es dans les mines de fer de Lorraine.
72. Gupta N, Quraishi M, Singh P, et al. (2017) Curcumine longa: Green and sustainable corrosion inhibitor for aluminum in HCl medium. *Anal Bioanal Electrochem* 9: 245–265.
73. Marc Fiquet SL, Loic Riou, Bernard Sanjuan (1997) caract risation des exc s d'aluminium dans les eaux superficielles de la martinique. pp. 31.
74. Kuyucak N (2000) Microorganisms, biotechnology and acid rock drainage—emphasis on passive-biological control and treatment methods. *Mining, Metallurgy & Exploration* 17: 85–95.
75. Chatain V (2004) Caract risation de la mobilisation potentielle de l'arsenic et d'autres constituants inorganiques pr sents dans les sols issus d'un site minier aurif re: Th se, Institut National des Sciences Appliqu es de Lyon.
76. Akil A, Hassan T, Lahcen B, et al. (2014) Etude de la qualit  physico-chimique et contamination m tallique des eaux de surface du bassin versant de Guigou, Maroc. *Eur Sci J* 10.
77. Newman DK, Kennedy EK, Coates JD, et al. (1997) Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. *Arch Microbiol* 168: 380–388.
78. Matera V (2001) Etude de la mobilit  et de la sp ciation de l'arsenic dans les sols de sites industriels pollu s: Estimation du risque induit: Pau.
79. Smedley PL, Kinniburgh D (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 17: 517–568.
80. Laperche V, Bod nan F, Dictor M, et al. (2003) Guide m thodologique de l'arsenic, appliqu    la gestion des sites et sols pollu s. *Rapport BRGM RP-52066-FR*.
81. Stollenwerk KG (2003) Geochemical processes controlling transport of arsenic in groundwater: a review of adsorption. *Arsenic in ground water*: Springer. 67–100.

82. Cullen WR, Reimer KJ (1989) Arsenic speciation in the environment. *Chemical reviews* 89: 713–764.
83. Inskeep WP, McDernlott TR, Fendorf S (2001) Arsenic (V)/(III) Cycling in Soils and Natural Waters: Chemical and Microbiological Processes. *Environmental chemistry of arsenic*: CRC Press. 203–236.
84. Fordham A, Norrish K (1979) Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. *Soil Research* 17: 307–316.
85. Livesey N, Huang P (1981) Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *Soil Sci* 131: 88–94.
86. Bowell R (1994) Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl Geochem* 9: 279–286.
87. Lin Z, Puls R (2000) Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. *Environ Geol* 39: 753–759.
88. Grosbois C, Schäfer J, Bril H, et al. (2009) Deconvolution of trace element (As, Cr, Mo, Th, U) sources and pathways to surface waters of a gold mining-influenced watershed. *Sci Total Environ* 407: 2063–2076.
89. Bossy A (2010) Origines de l'arsenic dans les eaux, sols et sédiments du district aurifère de St-Yrieix-la-Perche (Limousin, France): contribution du lessivage des phases porteuses d'arsenic: Université de Tours.
90. Shafer MM, Overdier JT, Hurley JP, et al. (1997) The influence of dissolved organic carbon, suspended particulates, and hydrology on the concentration, partitioning and variability of trace metals in two contrasting Wisconsin watersheds (USA). *Chem Geol* 136: 71–97.
91. Li X, Shen Z, Wai OW, et al. (2001) Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Marine Mar Pollut Bull* 42: 215–223.
92. Morgan JJ, Stumm W (1996) Aquatic chemistry: chemical equilibria and rates in natural waters: Wiley.
93. Swedlund P, Webster J (2001) Cu and Zn ternary surface complex formation with SO₄ on ferrihydrite and schwertmannite. *Appl Geochem* 16: 503–511.
94. Aranguren MMS (2008) Contamination en métaux lourds des eaux de surface et des sédiments du Val de Milluni (Andes Boliviennes) par des déchets miniers Approches géochimique, minéralogique et hydrochimique: Université Paul Sabatier-Toulouse III.
95. Karlsson T, Persson P, Skyllberg U (2005) Extended X-ray absorption fine structure spectroscopy evidence for the complexation of cadmium by reduced sulfur groups in natural organic matter. *Environ Sci Technol* 39: 3048–3055.
96. Cotton FA, Wilkinson G, Murillo CA, et al. (1988) Advanced inorganic chemistry: Wiley New York.
97. Ganjali MR, Esmaili BM, Davarkhah N, et al. (2017) Nano-molar Monitoring of Copper ions in Waste Water Samples by a Novel All-Solid-State Ion Selective Electrode (ASS-ISE). *Anal Bioanal Electrochem* 9: 187–197.
98. Bruland K, Lohan M (2006) Controls of trace metals in seawater. *The oceans and marine geochemistry* 6: 23–47.
99. Eary LE (1999) Geochemical and equilibrium trends in mine pit lakes. *Appl Geochem* 14: 963–987.

100. Baghdad B, Naimi M, Bouabdli A, et al. Evaluation de la contamination et évolution de la qualité des eaux au voisinage d'une mine abandonnée d'extraction de plomb; 2009.
101. Benzaazoua M (1996) Caractérisation physico-chimique et minéralogique de produits miniers sulfurés en vue de la réduction de leur toxicité et de leur valorisation.
102. Lghoul M (2014) Apport de la géophysique, de l'hydrogéochimie et de la modélisation du transfert en DMA: projet de réhabilitation de la mine abandonnée de Kettara (région de Marrakech, Maroc).
103. Esshaimi M, Ouazzani N, Valiente M, et al. (2013) Speciation of heavy metals in the soil and the tailings, in the zinc-lead Sidi Bou Othmane Abandoned Mine.
104. Bouabdli A, Saidi N, El Founti L, et al. (2004) Impact de la mine d'Aouli sur les eaux et les sédiments de l'Oued Moulouya (Maroc). *Bull Soc Hist Nat Toulouse* 140: 27–33.
105. Saidi N (2004) Le bassin versant de la Moulouya: pollution par les métaux lourds et essais de phytoremédiation.
106. El Hachimi ML, Fekhaoui M, El Abidi A, et al. (2014) Contamination des sols par les métaux lourds à partir de mines abandonnées: le cas des mines Aouli-Mibladen-Zeïda au Maroc. *Cahiers Agricultures* 23: 213–219.
107. Argane R, Benzaazoua M, Bouamrane A, et al. (2015) Cement hydration and durability of low sulfide tailings-based renders: A case study in Moroccan constructions. *Miner Eng* 76: 97–108.
108. El Hassani F, Boushaba A, Raï N, et al. (2016) Etude de la contamination par les métaux lourds des eaux et des sédiments au voisinage de la mine de Tighza (Maroc central oriental). *Eur Sci J* 12.
109. Farki K, Zahour G, Baroudi Z, et al. (2016) Mines et carrières triasico-liasiques de la région de Mohammedia: Inventaire, valorisation et étude d'impact environnemental. *Int J Innov Sci Res IJISR* 20: 306–326.
110. Taha Y (2017) Valorisation des rejets miniers dans la fabrication de briques cuites: Évaluations technique et environnementale: Université du Québec en Abitibi-Témiscamingue.
111. El Hachimi M, El Founti L, Bouabdli A, et al. (2007) Pb et As dans des eaux alcalines minières: contamination, comportement et risques (mine abandonnée de Zeïda, Maroc). *J Water Sci* 20: 1–13.
112. Elazhari A (2013) Etude de la contamination par les éléments traces métalliques des sédiments de l'oued Moulouya et de la retenue du barrage Hassan II en aval de la mine abandonnée Zeïda, Haute Moulouya: Université Cadi Ayyad, Faculté des Sciences et Techniques, Marrakech. 115 p.
113. El Hachimi ML, Bouabdli A, Fekhaoui M (2013) Les rejets miniers de traitement: caractérisation, capacité polluante et impacts environnementaux, mine Zeïda, mine Mibladen, Haute Moulouya (Maroc). *Environ Tech*: 32–42.
114. El Amari K, Valera P, Hibti M, et al. (2014) Impact of mine tailings on surrounding soils and ground water: Case of Kettara old mine, Morocco. *J. Afr. Earth Sci* 100: 437–449.
115. Nfissi S, Zerhouni Y, Benzaazoua M, et al. (2011) Caractérisation des résidus miniers des mines abandonnées de Kettara et de Roc Blanc (Jebilet Centrales, Maroc). *Société Géologique du Nord* 18: 43–53.
116. Ouakibi O, Loqman S, Hakkou R, et al. (2013) The potential use of phosphatic limestone wastes in the passive treatment of AMD: a laboratory study. *Mine water Environ.* 32: 266–277.

117. Hakkou R, Benzaazoua M, Bussi ère B (2008) Acid mine drainage at the abandoned Kettara mine (Morocco): 1. Environmental characterization. *Mine water Environ* 27: 145–159.
118. G ód éris (2002) Base de Donn ées Environnementales de Languedoc-Roussillon (Programme G ód éris 2002). 41.
119. Cartier A (1981) Etude de min éralisations à fluorine, barytine et sid érite en contexte hercynien: secteur du gisement d'Escaro (Pyr éni ès-Orientales): UER de sciences fondamentales et appliqu ées.
120. Banks D, Younger PL, Arnesen R-T, et al. (1997) Mine-water chemistry: the good, the bad and the ugly. *Environ Geol* 32: 157–174.
121. Stumm W, Morgan J (1981) An Introduction Emphasizing Chemical Equilibria in Natural Waters, Aquatic Chemistry. J. Wiley and Sons, New York. 2nd edition. A Wiley-Interscience Publication.
122. Brown M B, B. Wood, H. (2002) Mine water treatment technology, Application & Policy. London. 449.
123. Boon M, Heijnen JJ, Hansford G (1998) The mechanism and kinetics of bioleaching sulphide minerals. *Miner. Process Extr Metall Rev* 19: 107–115.



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