

Geochemical assessment and transfer of potential effects of metallic trace elements around abandoned mining sites in Kettara region (Morocco)

Lahcen Zouhri, Khalid El Amari, Mohamed Hibti, Abdelfattah Benkaddour, Adel Zghibi

▶ To cite this version:

Lahcen Zouhri, Khalid El Amari, Mohamed Hibti, Abdelfattah Benkaddour, Adel Zghibi. Geochemical assessment and transfer of potential effects of metallic trace elements around abandoned mining sites in Kettara region (Morocco). Ore and Energy Resource Geology, 2025, 18, pp.100076. 10.1016/j.oreoa.2024.100076. hal-04840151

HAL Id: hal-04840151 https://normandie-univ.hal.science/hal-04840151v1

Submitted on 16 Dec 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



FISEVIER

Contents lists available at ScienceDirect

Ore and Energy Resource Geology

journal homepage: www.sciencedirect.com/journal/ore-and-energy-resource-geology





Geochemical assessment and transfer of potential effects of metallic trace elements around abandoned mining sites in Kettara region (Morocco)

Lahcen Zouhri ^a, Khalid El Amari ^b, Mohamed Hibti ^b, Abdelfattah Benkaddour ^b, Adel Zghibi ^{c,d,*}

- a AGHYLE, Institut Polytechnique UniLaSalle Beauvais, SFR Condorcet FR CNRS 341719, rue Pierre Waguet, F-60026 Beauvais Cedex, France
- b Laboratory of Georesources, Geoenvironment and Civil Engineering, Faculty of Sciences and Technologies Marrakech (FSTM), Cadi Ayyad University, Boulevard Abdelkrim Al Khattabi. BP 549, 40000 Marrakech. Morocco
- ^c College of Science and Engineering, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar
- d LR01ES06 Laboratory of Geological Resources and Environment, Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, Tunis, Tunisia

ARTICLE INFO

Keywords: Mine environment Metallic trace elements Soil contamination, groundwater Morocco

ABSTRACT

The degradation of environmental quality due to pollution is a pressing concern worldwide, particularly in areas that have been abandoned after mining activities. One significant aspect of this degradation is the contamination of soil and water resources by Metallic Trace Elements (MTE). These elements, originating from mining operations, pose serious environmental and human health risks, necessitating urgent attention and remediation efforts. Understanding the characteristics and extent of MTE contamination in abandoned mining areas is crucial for effective environmental management and sustainable development. In this context, this study aims to investigate the patterns, distribution, and impacts of MTE contamination in soil and water resources within Kettara abandoned mining areas (Morocco), offering insights into potential mitigation strategies and policy interventions to address this critical environmental issue. Stream and groundwater samples were collected in the Kettara region where the abandoned tailings constitute with Acid Mine Drainage (AMD), the principal source of this contamination. Stream samples were collected in 2018 at fourteen points near sixteen hydrogeological wells and situated at different distance from the pollution source.

This study addresses an environmental concern, focusing on the dispersion of MTE such as Arsenic, Zinc, and Nickel in both streams and groundwater. Through geochemical analysis, it is revealed that Arsenic is particularly prevalent, with higher concentrations detected in streams, especially those proximate to mining waste sites. The main sampling water near the abandoned mine shows several anomalies (As, Ni and Zn). The higher As concentration in the stream samples E1 and E2 with 179.55 and 96.63 ppm and near the mine wastes. The concentration of As is also higer in the water samples especially in the hydrogeological well P21 and P2 with 9.665 and 7.798 ppm.

The presence of MTE in groundwater is linked to various factors, including the direction of flow (vertical or lateral) from soil to groundwater and the hydraulic conditions (presence of the drainage axis that is materialized by the convergence of the groundwater flow from the upstream to the downstream, generally from the hydrogeological wells P1 to P23). The hydraulic relationship between streams and groundwater, hydrogeological properties such as aquifer porpermeability (vertical scale 2.5×10^{-14} to 1.31×10^{-12} m/s and horizontal scale 9×10^{-14} to 0.37×10^{-9} m/s) and transmissivity (about 10^{-2} m²/s), and the configuration of the piezometric geometry (including the presence of drainage axes and divisional boundaries within the Ketarra groundwater) are factors that contribute to the mobility and distribution of MTE within the water resources of the Kettara basin.

E-mail addresses: azghibi@hbku.edu.qa, adel.zghibi@fst.utm.tn (A. Zghibi).

^{*} Corresponding author.

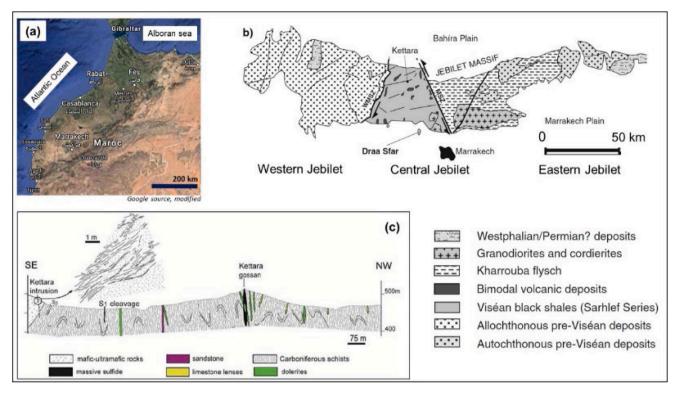
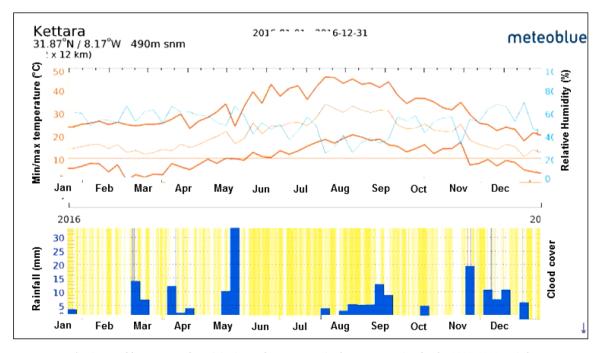


Fig. 1. Location map of the Kettara region; (b) Geological sketch map of the Jebilet massif (modified from Huvelin, 1977; N'diaye et al., 2016) and (c) geological cross-section of the study area (N'diaye et al., 2016).



 $\textbf{Fig. 2.} \ \ \textbf{Monthly averages of precipitation and temperature in the Kettara station for the 2008-2019 period.}$

1. Introduction

Abandoned mines represent a principal threat to the environment (sediments, streams, air, surface water, and groundwater). Environmental consequences are not negligible in terms of public health and the protection of biodiversity and the ecosystem. In the mining context, AMD is identified as a contributing factor to the sediments, stream and water degradations facto that are studied in the multidisciplinary works

in terms the environmental and economic impact (Worlanyo and Jiangfeng, 2021), geochemical aspects especially of sulphide mine tailings (Lindsay et al., 2015; Blowes et al., 1998) and eco-toxicological impact (Equeenuddin et al., 2010; Buzatu et al., 2016; Estrades et al., 2016; Han et al., 2017, Yang et al., 2017). The evaluation of the soil quality is considered as a principal component in the comprehension of the MTE mobility and depends to the nature of contaminants indicators in the international mining site: Morocco (El Amari et al., 2014; Moyé

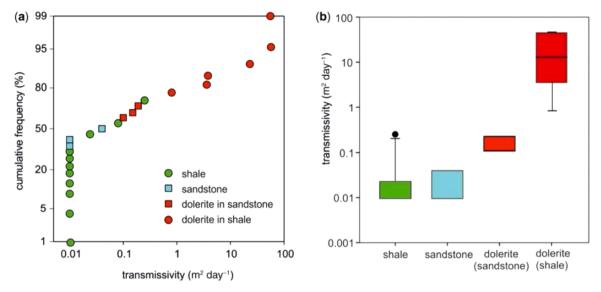


Fig. 3. Transmissivity data from pumping tests from boreholes encountering shale, fine-grained sandstone, and dolerite intrusions in the Benue Trough. (a) Cumulative frequency plot. (b) Box plot (Macdonald and Davies, 2019).

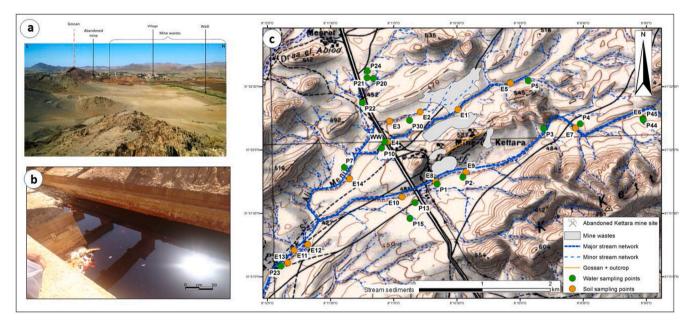


Fig. 4. (a) Location of the abandoned mine infrastructures of the Kettara basin; (b) Acid Mine Drainage observed the mine site; (c) Stream sediment and groundwater sampling map in the abandoned Kettara mine (Zouhri et al., 2019, modified).

et al., 2017), China (Teng et al., 2014), Swiss (Blaster et al., 2000); Spain (Chopin and Alloway, 2007).

The consequence of this contamination is related to the dispersion of the principal MTE in the river and the groundwater. Indeed, under weather conditions, mining wastes are ready to leach and migrate to the roots of soil, and groundwater. These components are considered the main cause of human vulnerability to contaminants (Souza et al., 2017; Khan et al., 2013; Zouhri et al., 2019).

In Moroccan abandoned mines such as Kettara (Fig. 1), the lithological factor and especially the interaction water-rock, play an important role in the comprehension of the degradation of the soil and water quality (El Amari et al., 2014; Moyé et al., 2017). The mine tailings are considered a source of pyrite, pyrrhotite, galena, and chalcopyrite which take direct link to these MTE. Indeed, the soil of the abandoned mine of the Kettara has been subjected of the groundwater quality in the fissured media (Moyé et al., 2017) and the bacteriological features in the

semi-arid climate (Zouhri et al., 2019). Therefore, the abandoned site of the Kettara basin becomes and environmental and experimental site of the geochemical, hydrogeological and bacteriological investigations.

In the Kettara basin, the environmental monitoring of sediments and groundwater quality is very important where the groundwater resources are used by the local population and especially in agricultural activities. Therefore, in order to assess the water resource in the study area, multidisciplinary research should be conducted.

In this study, a new geochemical investigation of the stream and near the hydrogeological wells has been realized in order to better (i) define the presence of the MTE in the stream, (ii) qualify the transfer from stream to groundwater with the vertical and horizontal hydraulic components, (iii) characterize the geochemical and hydrogeological relation between upstream and downstream, and (iv) to take other factors explaining the MTE dispersion which are governing by meteorological conditions.

Table 1.1Trace elements analyzed in water samples expressed in ppb obtained at 15 sampling points.

Piezo ID	24Mg (ppb)	39K (ppb)	44Ca (ppb)	45Sc (ppb)	48Ti (ppb)	51V (ppb)	52Cr (ppb)
P1	16,240	937.2	53,820	2.946	207.2	1.056	0.628
P2	16,510	3594	51,690	2.695	201.8	1.24	0.768
P3	13,800	1935	52,140	2.187	202	0.8	0.462
P4	17,770	2017	53,280	4.431	207.2	1.203	0.996
P5	16,580	1109	51,830	2.245	200.1	1.383	0.57
P7	125,900	2616	418,000	2.788	1666	2.008	0.505
P10	216,200	1969	596,900	2.803	2611	0.558	1.289
P13	33,700	2281	90,670	2.236	349.6	1.857	0.767
P15	28,050	1909	72,550	2.317	278.6	3.67	0.572
P20b	64,030	3610	112,400	2.012	434.3	1.227	0.697
P22	46,070	1717	97,970	2.057	378.4	2.784	0.489
P23	52,360	2151	191,200	2.146	749.1	2.396	2.07
P30	219,800	1404	613,200	2.659	2675	0.806	1.286
P44	18,680	1013	51,330	1.812	201.3	1.18	0.658
P45	19,640	991.9	52,830	1.862	202.7	2.925	1.965

2. Materials and methods

2.1. Hydrological setting of the abandoned mine of Kettara

The particularity of Kettara mine occupies an important geographical position in Morocco and considering its proximity to Marrakech is the fourth largest city in the Kingdom of Morocco (The saturated zone of the abandoned mine of the Kettara is a). In terms of climatic context, undergoes a continental semi-arid climate which is hot and dry in the summer. The meteorological data delivered by Meteoblue indicates that rainfall is about 250 mm/y and shows an irregularity of the precipitation repartition. Indeed 520 mm is considered as peaks that are recorded in 2009 and 2010. The average temperature value in the region is about 20 °C (Fig. 2).

The geological have been described in numerous works (El Amari et al., 2014; N'Diaye et al., 2016; Moyé et al., 2017; Zouhri et al., 2019). The Kettara mine geology is very complex because it is considered a structural element of the Central Jebilet domain (The saturated zone of the abandoned mine of the Kettara is b). One finds in this domain the metamorphosed volcano-sedimentary formations of the Upper Visean to Westphalo-Permian (Huvelin, 1977) and mainly the shales of Sarhlef. The second formation which belongings to the uppermost Carboniferous magmatic series is exposed in veins, plutons, sills, and dykes (Huvelin, 1977).

The principal aquifers are represented by the Sarhlef shale and granite units of the Central Jebilet (The saturated zone of the abandoned mine of the Kettara is b,c). In this study, the geochemical, geological and hydrogeological investigations are concerned especially with the major shale deposits which are characterized by the network of fractures and

the hydraulic repartition of the abandoned mine of the Kettara (Zouhri et al., 2019). Indeed, Essaifi et al. (2001) indicate that the first formation is materialized by schistosity of the NNE-SSW direction within a low metamorphism degree (Le Corre and Saquaque, 1987). For the second formation formed by Uppermost Carboniferous magmatic series, the mafic and felsic magmatism is identified in the area within an orientation of the magmatic veins and especially N0-N40 and N60-N80 (Youbi et al., 2001).

The saturated zone of the abandoned mine of the Kettara is dominated by shale deposits. The hydrogeological system is composed of the superficial aquifer characterized by altered shales and deep hydrogeological units. The particularity of this system is materialized by the repartition of discontinuities and fractures network in the shale formations (Moyé et al., 2017). Advancements in petroleum technologies especially using hydraulic fracturing and horizontal drilling show a particularity of shale reservoirs (Goral et al., 2020). Petrophysics investigations which are realized for the variable hydrocarbons in the shale formation allow defining a low permeability (less than 1000 nD) and a low porosity (typically less than 5 % (Goral et al., 2020). In the other works about the Silurian shales (Cao et al., 2015), hydrogeological tests indicate that the porosity in this formation varies between 3.65–18.26 %.

The transmissivity, obtained by pumping tests in the shale aquifer, is about 10^{-2} m²/s (Fig. 3) (MacDonald et al., 2005).

In the Maquoketa shale formations, laboratory Measurements on the Rock shale Core show a similar hydrodynamic value which they are within ranges given in the literature by Domenico and Schwartz (1998) and Neuzil (1994). The vertical core scale hydraulic conductivities ranged in value from 2.5×10^{-14} to 1.31×10^{-12} m/s. The horizontal core scale hydraulic conductivities ranged in value from 1.9×10^{-14} to 0.37×10^{-9} m/s. Effective porosity ranges between 0.04 and 0.26. Although these values are extremely small, particularly hydraulic conductivity, they are within ranges given in the literature by Domenico and Schwartz (1998) and Neuzil (1994).

The presence of the MTE in the soil, sediments and water result mainly from several factors, urban, industrial (mining exploration) and agricultural activities (Liu et al., 2021). MTE sources are often associated with health risks (for example MTE Toxicity is identified in Fishes with consequent impact on the behavioral, reproductive, physiological, and developmental functions). However, the presence of the MTE can be related the natural interaction between water infiltration of the geological formation.

2.2. Geochemical analysis and data treatment

In this study, a new geochemical investigation could give more information about the groundwater quality and the relationship between sediments and the groundwater of the abandoned of the Kettara and

Table 1.2Trace elements analyzed in water samples expressed in ppb obtained at 15 sampling points.

Piezo ID	63Cu (ppb)	64Zn (ppb)	75As (ppb)	88Sr (ppb)	98Mo (ppb)	121Sb (ppb)	208Pb (ppb)	232Th (ppb)	238U (ppb)
P1	3.905	7.096	3.119	281.9	6.716	0.412	0.346	0.175	1.54
P2	4.828	298.9	1.915	267.7	4.86	0.425	0.156	0.18	1.689
P3	3.431	139.7	1.151	292.5	3.714	0.303	0.152	0.132	1.664
P4	6.863	135	1.803	235.5	4.691	0.306	0.089	0.214	2.065
P5	5.255	12.04	1.523	232.9	3.153	0.103	0.14	0.126	1.013
P7	3.098	28.13	1.975	2801	1.014	0.094	0.179	0.06	9.888
P10	3.937	34.2	0.644	3329	0.129	0.13	0.26	0.067	5.515
P13	3	20.48	1.029	503.6	1.733	0.141	0.164	0.029	3.532
P15	3.289	15.57	1.724	435.6	1.891	0.116	0.185	0.02	3.824
P20b	5.633	64.2	1.423	592.5	2.255	0.127	0.127	0.031	4.999
P22	4.156	6.54	2.149	586.8	3.355	0.063	0.097	0.034	3.468
P23	3.385	17.46	1.173	1072	1.007	0.085	0.176	0.032	4.441
P30	2.946	32.4	0.649	4412	ND	0.09	0.04	0.057	6.298
P44	2.703	5.048	0.981	254	4.077	0.056	0.076	0.021	1.875
P45	2.511	5.563	1.715	247.1	3.913	0.077	0.214	0.02	1.763

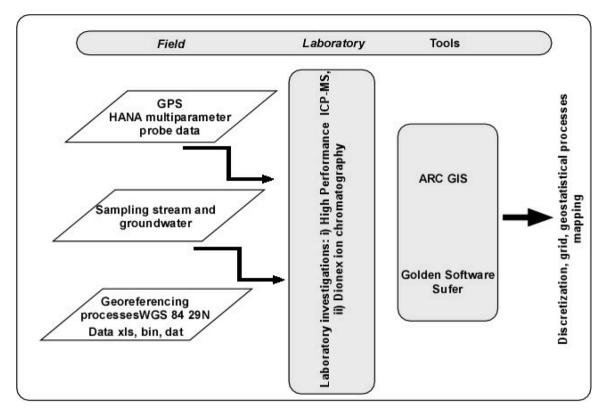


Fig. 5. Methodology and multidisciplinary approaches used in the case of the abandoned mine of Kettara basin.

especially at the downstream of the village and the tailings (Fig. 4a). A geochemical and hydrochemical sampling campaign was realized in the period between 18 and 22 September 2017. 14 stream sediments (E) near 16 wells (P) and located both upstream and downstream of the Kettara mine tailings (Table 1.1, Fig. 4).

Table 1.2

Multidisciplinary approach was conducted in the field and in the laboratory investigations (Fig. 5) The georeferencing of stream sampling points and hydrogeological wells was been realized by using GPS Garmin Extrex of the Institut Polytechnique UniLaSalle. The measurement of the physico-chemical parameters (Temperature (T), pH, Total Dissolved Solids (TDS), groundwater level, Alcalinity, Conductivity, resistivity of the water were collected directly in the hydrogeological wells by using the HANA multiparameter probe.

Geochemical parameters, MTE (for stream sediments and ground-water) and ions (anions and cations) were characterized by the Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) for over 50 elements. But in this study, we will focus on Zn, As, and Ni for stream sediments. Dionex ICS chromatography technics carried out at the UniLaSalle laboratory (Beauvais, France) for cations and anions analyses of groundwater (Ca²⁺, Mg²⁺, Cl⁻, NO³⁻, PO₄²⁻ and SO₄²⁻).

The interpretation and mapping were realized by Geographical Information System (ArcGis) and Golden Software surfer. Hydrogeologic and Geochemical equipments are located in the plateform of the Institut Polytechnique UniLaSalle (Beauvais, France). In term of the MTE, 55 elements were analyzed the most principal of which Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Be, *Sc*, Ti, V, Se, Sr, Y, Mo, Cd, Sb, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Th, U, Al, P and K. Dionex ICS" which employed at the UniLaSalle laboratory allows to determine cations and anions analyses: Ca²⁺, Mg²⁺, Cl⁻, NO³⁻, PO₄²⁻ and SO₄²⁻.

3. Results and discussions

3.1. Groundwater flow

The characterization of the transfer of contaminants needs to identify the electrical conductivity and the groundwater flow in this fissured shale system. Electrical conductivity values are characterized by a spatial variation in the groundwater within a higher value in the central part of the North-West study area: 3481 $\mu s/cm$ in P10.The hydrogeological campaign of 2017 allows determining the groundwater level in the hydrogeological wells (Fig. 6). In the upstream of the Kettara basin, the hydraulic head is greater than 480 m (northeast zone) against 400 m downstream of the basin (South-West of the abandoned mine). Generally, and in this system, the groundwater flows from North-East to the South-West and North-West direction.

The analysis and the interpretation of the groundwater flow map reveal the identification the drainage axis (Fig. 6) which materialized by the convergence of the groundwater flow from the upstream to the downstream (generally from P1 to P23). A second identification is materialized by the presence in the fissured shale system of the dividing axis in the north and in the south of the Kettara basin (generally between P22 and P24, P13 and P15 respectively).

3.2. Metallic trace elements analysis

The analysis and the interpretation of the spatial distribution of MTE especially in stream samples and in the hydrogeological wells reveal a migration of the contaminants from the soil to saturated zone in according to the vertical and horizontal components from the upstream to downstream of the groundwater. This contamination is expressed especially by the arsenic, zinc and nickel.

The As element is identified with higher concentration in the stream and especially in the samples E1 and E2 with 179.55 and 96.63 ppm respectively. Theses samples are located near the mine wastes. This element reveals a significant concentration especially in the North-West

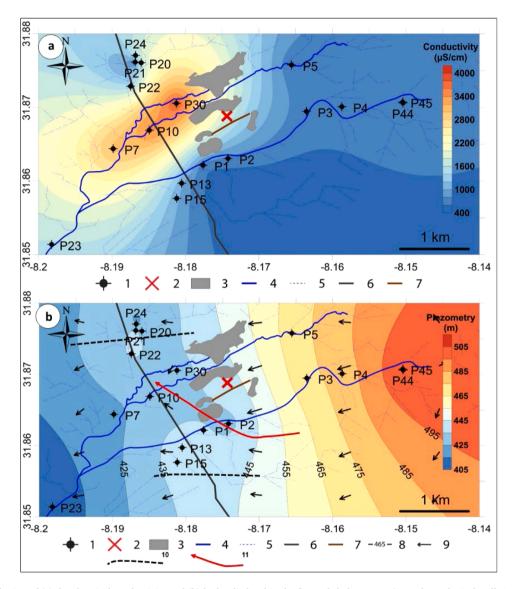


Fig. 6. Spatial distribution of (a) the electrical conductivity and (b) hydraulic head in the fissured shale system. (1. Hydrogeological well; 2. Kettara mine; 3. Mine wastes; 4. Stream networks; 5. Minor stream networks; 6. Roads; 7. Gossan outcrop; 8. Isopieze curves; 9. Groundwater flow; 10. Dividing axis; 11. Drainage axis) (Zouhri et al., 2019, modified).

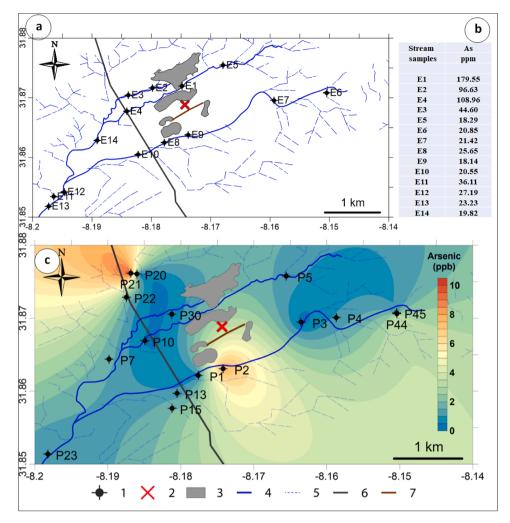


Fig. 7. (a) and (b) Stream sampling location and Arsenic value and (c) spatial distribution of arsenic in the stream sediments in abandoned Kettara area (1. Hydrogeological well; 2. Kettara mine; 3. Mine tailings; 4. Stream networks; 5. Minor stream networks; 6. Main roads; 7. Gossan outcrop).

of the sector but near of the stream sample (about 1 km to E1). Two higher concentrations of As were been identified in the groundwater samples, especially in the hydrogeological well P21 and P2 with 9.665 and 7.798 ppm, respectively.

The MTE results about Zinc (Zn) concentrations reveal the high values in the stream sediments (greater than 134 ppm) are in E1 to E4 (Fig. 8). The richness of zinc in this zone is due to its position near downstream of the tailings. However, the high Zn concentrations in groundwater are not at the same location; they are recorded in the hydrogeological wells located in the center upstream and the downstream of the basin especially in P4, P2, P15 and P7, respectively.

The MTE investigations about Ni concentrations indicate high values especially in the south of left bank of the stream. In the upstream, samples E12 and E13 recorded 93.25 and 87.85 ppm respectively. E8, E9, and E10 have also important values of 81.98; 74.29 and 87.57 ppm, respectively (Fig. 9).

In according to the stream left bank and in the upstream, the Ni concentration is lower and values are about 60 ppm. The hydrogeochemical state of the groundwater is inverse in this location (south of the left bank of the stream). Indeed, the hydrogeological wells reveal lower concentration against stream samples except in the P4, P7, and P15 groundwater samples with 0.56; 0.1, and 0.04 μ g/L, respectively.

The infiltration of the Arsenic from stream samples (E2 and E3) (Fig. 7a) near the mine tailings towards groundwater is accompanied by a lateral movement. This groundwater transfer to the hydrogeological wells in P20 and P21 (Fig. 7b) is induced by the groundwater pumping in

the area. The presence of the dividing axis in the north-west area could approve this circulation. In term of the As concentration, the Directive requirements and the World Health Organization (WHO) guidelines recommends that the arsenic level in drinking water, should be $<10\,\mu\text{g}/$ L. Hydrogeological well P21 is 1000 times over this limit (10,000 $\mu\text{g}/\text{L}$).

The second factor which can explain the As contamination is characterized by the presence of AMD. This environmental phenomenon which is typical to the abandoned mine is related especially to the exposition of the sulfide-bearing to the oxygen and water. The oxidation of the sulfide constitutes the principal geochemical process (Sima et al., 2011; El Amari et al., 2014; Pyatt and Grattan, 2001) and sulfidic mine tailings are identified as the major source of hazardous materials leading to the degradation of the surficial and groundwater ressources (Zouhri et al., 2019). It is likely that this contamination is linked to the liberation and transport of the MTE elements (especially As element) in mine tailings. This mobility has been confirmed in other study under arid and continental climate (Sima et al., 2011; Smuda, 2009; Smuda et al., 2008). Geochemical evolution in the stream and AMD in the mine environment have been studied in many research works: i) the AMD and consequence which are expressed by the environmental impact on the soil and the water resources (Cidu et al., 2011); ii) the eco-toxicological assessment of stream water and groundwater (Han et al., 2017).

Certainly, the water-rocks interaction can give more information about the As contamination in the groundwater samples. Indeed, the occurrence of geogenic arsenic in groundwater is of major concern in fractured crystalline bedrock aquifers, in particular for rural regions that

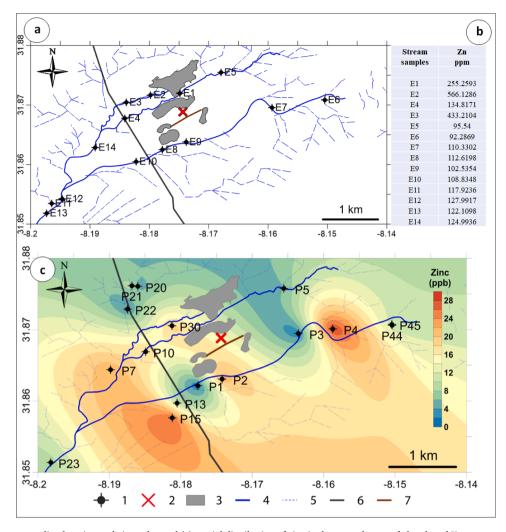


Fig. 8. (a) and (b) Stream sampling location and zinc value and (c) spatial distribution of zinc in the groundwater of abandoned Kettara area (c) (1. Hydrogeological well; 2. Kettara mine; 3. Mine tailings; 4. Stream networks; 5. Minor stream networks; 6. Roads; 7. Gossan outcrop).

rely on private bedrock wells for their domestic water supply (Ryan et al., 2013; Zheng and Ayotte, 2015).

Arsenic is a ubiquitous element of the Earth's crust and its chemical species are volatile and highly soluble (Masuda, 2018) in water environment. This volatility can be proceeded in the vadoze zone. The evaluation of the arsenic fluxes reservoirs at the Earth's surface indicates that anthropogenic activities play an important role in dispersing arsenic pollution to the atmosphere, pedosphere and hydrosphere (Fig. 10). Fluxes from river into aquifers depends to the hydrogeological relationship between rivers and hydrogeological reservoir within the influence of the recharge parameter. This relation facilitates the migration of the Arsenic especially to the less deep aquifer and fractured media.

Hight concentration of the Zn in the north-west in the samples stream could not explain the vertical movement towards the unsaturated and saturated zones. Indeed, high concentration is identified in the groundwater samples in the upstream of the groundwater towards the downstream. Lateral flow of the Zn concentration in the shale aquifer is probably related to the atmospheric dispersion (wind movement, weathering conditions like as As contaminant) (Fig. 10). This zonation of the Zn contamination and its lateral mobilization processes are already identified in Belgium sites (Bas et al., 1990). In terms the hydrodynamic and physico-chemical processes, Zn element is strongly adsorbed to soils at or more than 5. In comparison with numerous work, this element is characterized by low mobility especially in most soils (Christensen et al.,

1996; Gao et al., 1997).

In other works, It has been demonstrated that the Zn element is also identified in water resources and in the surface (Noulas et al., 2018). The presence of the Zn element nd its contact with the environment are linked to the principal sources including municipal wastes, urban runoff, industrial activities and mine drainage. Indeed, the erosion sediments (Liu et al., 2021) especially of soil particles constitutes the major action improving the dispersion of Zn with the support of the wind.

It is considered that the atmospheric input of heavy metals is probably responsible for the locally high zinc concentrations in groundwater. MTE dispersion, especially the arsenic is approved by numerous works that are driven by into account the meteorological simulations in order to predict the transport and dispersion of As in the south-western Europe (Chen et al., 2012).

The analysis and the interpretation of the distribution of the Ni concentration does not highlight any relationship between the stream and groundwater contamination. A mixture of ferrous and nonferrous metal properties has been exhibited by the Nickel which is considered as a transition element. This mixture reveals two associations: with iron indicates (siderophine) and with sulfur (chalcophile). Two deposits can explain the origin of Nickel concentration: (1) the alteration of the shale formation involving the laterites where nickeliferous limonite [(Fe,Ni)O (OH)] constitutes the major ore minerals and (2) the presence of the magmatic sulfide deposits in the study area can explain the presence of nickel and especially the pentlandite [(Ni,Fe)₉S₈].

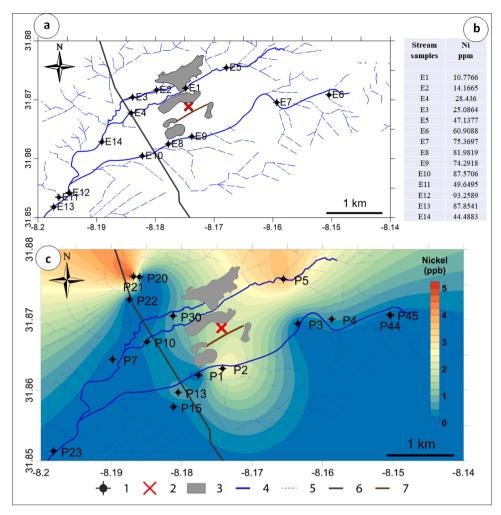


Fig. 9. (a) and (b) Stream sampling location and Nickel value and (c) spatial distribution of Nickel in the groundwater of abandoned Kettara area (c) (1. Hydrogeological well; 2. Kettara mine; 3. Mine tailings; 4. Stream networks; 5. Minor stream networks; 6. Roads; 7. Gossan outcrop).

The contamination in the groundwater especially in the north-west of the study area is explained by the presence of the Mesret fault activity in the vicinity of the P21 and 22.

The deposits are associated with basic magmatic (gabbros) or ultrabasic (picrites, komatiites) rocks (Santarelli, 2007). Among the most important are:(i) deposits associated with the intrusive basic magmatic complex in the Archean and Proterozoic of Sudbury (Canada); (ii) deposits associated with the gabbros / peridotite alternations of Bushweld (South Africa), and Stillwater (Montana USA); (iii) deposits associated with doleritic intrusions in relation to thick permo-Triassic continental basalts: Norilsk–Talnakh (Siberia) and (iv) deposits associated with Archean komatiites: Australia W (Kambalda), Canada (Quebec), Zimbabwe.

This study has limitations with regard to climate change. It is very important to check the concentrations and anomalies identified in this study against the low and high-water periods. The research work carried out in this project requires both qualitative and quantitative monitoring. Automatic probes for continuous monitoring of water levels, hydrochemical parameters and MTE analysis require financial resources, which we would like to request from the Europe–Maghreb department.

4. Conclusion

The assessment of potential sources of contaminants, including Arsenic (As), Zinc (Zn), and Nickel (Ni), is conducted across various sample types, encompassing streams, soil sediments, and groundwater

within the abandoned mine of the Kettara basin. The relationship between stream and groundwater quality extends beyond Acid Mine Drainage (AMD) alone, encompassing factors such as vertical transfer from soil to groundwater within the shale aquifer, interactions between rock and water resources, the network of fractures, and dispersion influenced by meteorological conditions. Hydrogeological characteristics such as transmissivity, porosity, and hydraulic conductivity offer valuable insights into the behavior and transfer of contaminants within shale systems, influenced by the degree of fracturation networks. Additionally, future work will involve conducting pumping tests to facilitate the development of numerical models, enabling the tracking of groundwater flow within fractured media and the movement of MTE. Given the significant reliance on groundwater for drinking water and agricultural activities in the vicinity of the abandoned mine environment, it is imperative to establish an expert commission in collaboration with Moroccan authorities to establish standards for contaminants in soil and groundwater, benchmarked against European counterparts. Environmental and scientific recommendations will be crucial for mitigating the exposure to MTEs such as Lead (Pb), Zinc (Zn), and Arsenic (As) in both soil and groundwater resources. The environmental ramifications are evident in agricultural practices reliant on irrigation, necessitating careful consideration of public health concerns within water governance discussions.

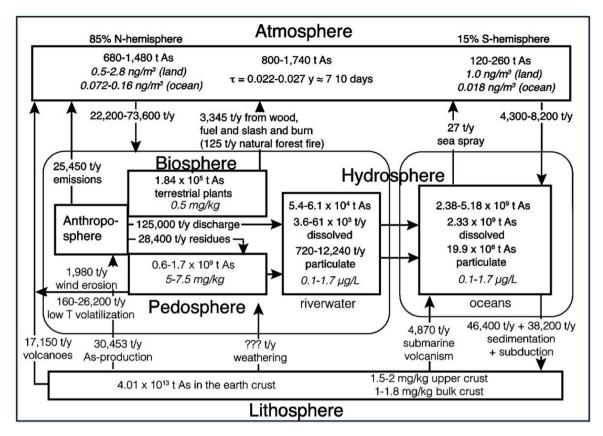


Fig. 10. Global arsenic cycle. Reservoir sizes and Fluxes in different parts of the geosphere (Matschullat, 2000).

CRediT authorship contribution statement

Lahcen Zouhri: Writing – original draft, Methodology, Investigation, Funding acquisition, Conceptualization. Khalid El Amari: Writing – review & editing, Methodology, Formal analysis. Mohamed Hibti: Writing – review & editing, Methodology, Formal analysis, Conceptualization. Abdelfattah Benkaddour: Writing – review & editing, Methodology, Adel Zghibi: Writing – review & editing, Methodology, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful to the collaboration between the "Institut Polytechnique UniLaSalle" and the "FST- Cadi Ayyad University of Marrakech (Morocco)". The authors wish to express their gratitude to students of the PA2 "Hydrogéologie & Risques Naturels"- G078 class.

This publication was made possible by BFC grant #BFC04–0719–200004 from the Qatar National Research Fund (a member of Qatar Foundation). The findings herein reflect the work, and are solely the responsibility of the authors.

Data availability

Data will be made available on request.

References

Bas, G., Pedroli, M., Maasdam, W.A.C., Verstraten, J.M, 1990. Zinc in poor sandy soils and associated groundwater. A case study. Sci. Total. Environ 91, 59–77.

Blaster, A., Smith, J., Müller, K., 2000. Evaluation of contaminant indicators in international mining sites: a case study from Switzerland. J. Environ. Stud. 45, 123–135.

Blowes, D.W., Jambor, J.L., Hanton-Fong, C.J., Lortie, L., Gould, W.D., Geochemical, 1998. mineralogical and microbiological characterization of a sulphide-bearing carbonate-rich gold-mine tailings impoundment, Joutel, Québec. Applied Geochemistry 13 (6), 687–705.

Buzatu, A., Dill, H.-G, Buzgar, N., Damian, G., Apopei, Maftei A.-E., 2016. Efflorescent Sulfates from BaiaSprie Mining Area (Romania) - Acid Mine Drainage and Climatological Approach. Sci. Total. Environ 542, 629–641.

Cao, T., Song, Z., Wang, S., Cao, X., Li, Yan, Xia, Jia, 2015. Characterizing the pore structure in the Silurian and Permian shales of the Sichuan Basin, China. Mar. Pet. Geol 61, 140–150.

Chen, B., Stein, A.F., Castell, N., de la Rosa J. D. Sanchez de la Campa, A.M., Gonzalez-Castanedo, Y., Draxler, R.R., 2012. Modeling and surface observations of arsenic dispersion from a large Cu-smelter in southwestern Europe. Atmospheric Environment 49, 114–122.

Christensen, J., Jensen, D., Christensen, T., 1996. Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. Water Research 30, 3037–3049.

Chopin, E.I.B., Alloway, B.J., 2007. Trace element partitioning and soil particle characterisation around mining and smelting areas at Tharsis, Ríotinto and Huelva. SW Spain Sci. Total Environ. 373, 488–500. https://doi.org/10.1016/j. scitotenv.2006.11.037.

Cidu, R., Frau, F., Da Pelo, S, 2011. Drainage at abandoned mine site: natural attenuation of contaminants in different seasons. Mine Water & Envir 30, 113–126. https://doi. org/10.1016/j.jclepro.2012.02.016.

Domenico, P.A., Schwartz, F.W., 1998. Physical and Chemical Hydrogeology. Wiley, New York, p. 505 p.

El Amari, K., Valera, P., Hibti, M., Pretti, S., Marcello, A., Essarraj, S, 2014. Impact of mine tailings on surrounding soils and ground water: case of Kettara old mine. Morocco. J. Afr. Earth Sci. 100, 437–449.

Equeenuddin, M., Tripathy, S., Sahoo, P., Panigrahi, M., 2010. Geochemistry of ochreous precipitates from coal mine drainage in India. Environ. Earth Sci. 61, 723–731. https://doi.org/10.1007/s12665-009-0386-9.

Essaifi, A., Lagarde, J.L., Capdevilla, R., 2001. Deformation and displacement from shear zone patterns in the Variscan upper crust (Jebilet, Morocco). J. Afr. Earth Sci. 32, 335–350

- Estrades, C., Llambí, C., Perera, M., Rovira, F., 2016. Large-scale mining in a small developing country: macroeconomic impacts of revenue allocation policies. Resources Policy 49, 433–443. Pages.
- Gao, S., Walker, W., Dahlgren, R., et al., 1997. Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. Water Air and Soil Pollution 93, 331–345.
- Goral, J., Panja, P., Deo, M., Andrew, M., Linden, S., Schwarz, J.-O., Wiegmann, A., 2020.
 Confinement Effect on Porosity and Permeability of Shales. Scientific Reports (10), 49
- Han, Y.-S, Youm, S.-J, Oh, C., Cho, Y.-C, Ahn, J.-S., 2017. Geochemical and ecotoxicological characteristics of stream water and its sediments affected by acid mine drainage. Catena 148 (1), 52–59.
- Huvelin, P., 1977. Étude géologique et gîtologique du massif hercynien des Jebilet (Maroc occidental). Notes et Mém. Serv. Géol. Maroc 232, 307 bis.
- Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M.T., 2013. Drinking water quality and human health risk in Charsadda district, Pakistan. J. Clean. Prod 60, 93–101
- Le Corre, C., Saquaque, A, 1987. Comportement d'un système pluton-encaissant dans un champ de déformation régional; le granite du Bramram (Jebilet, Maroc hercynien). Bull. Soc. Géol. 3 (4), 665–673. Fr.
- Lindsay, M.B.J, Moncur, M.C., Bain, J.G., Jambor, J.L., Ptacek, C.J., Blowes, D.W., 2015. Geochemical and mineralogical aspects of sulfide mine tailings. Appl. Geochem. 57, 157–177.
- Liu, Y., Wang, P., Gojenko, B., Yu, J., Wei, L., Luo, D., Xiao, T, 2021. A review of water pollution arising from agriculture and mining activities in Central Asia: facts, causes and effects. Environ. Pollut. 291, 118209. https://doi.org/10.1016/j. envpol.2021.118209. Dec 15Epub 2021 Sep 21. PMID: 34563852.
- Macdonald, A.M, Davies, J., 2019. Fractures in shale: the significance of igneous intrusions for groundwater flow. In: Ofterdinger, O, MacDonald, A.M, Comte, J.-C, Young, M.E (Eds.), Groundwater in Fractured Bedrock environments: Managing Catchment and Subsurface Resources. Geological Society of London, 71-79. Geological Society Special Publication, London, UK, p. 479.
- MacDonald, A.M., Kemp, S.J., Davies, J., 2005. Transmissivity variations in mudstones. Ground Water 43 (2), 259–269.
- Masuda, H., 2018. Arsenic cycling in the Earth's crust and hydrosphere: interaction between naturally occurring arsenic and human activities. Prog. Earth Planet Sci. 5, 68. https://doi.org/10.1186/s40645-018-0224-3.
- Matschullat, J., 2000. Arsenic in the geosphere: a review. Sci. Total Environ. 249, 297–312. https://doi.org/10.1016/S0048-9697(99)00524-0.
- Moyé, J., Picard-Lesteven, T., Zouhri, L., El Amari, K., Hibti, M., Benkaddour, A., 2017. Groundwater assessment and environmental impact in the abandoned mine of Kettara (Morocco). Environ. Poll. 231 (Pt 1), 899–907.
- N'Diaye, A., Mijouin, L., Hillion, M., Diaz, S., Konto-Ghiorghi, Y., Percoco, G., Chevalier, S., Lefeuvre, L., Harmer, N.J., Lesouhaitier, O., Feuilloley, M.G., 2016. Effect of substance P in Staphylococcus aureus and Staphylococcus epidermidis

- virulence: implication for skin homeostasis. Front. Microbiol. 7, 506. https://doi.org/10.3389/fmicb.2016.00506.
- Neuzil, C.E., 1994. How permeable are clays and shales? Water Resour. Res. 30 (2), 145–150.
- Noulas, C., Tziouvalekas, M., Karyotis, T., 2018. Zinc in soils, water and food crops. J. Trace Elements Med. Biol. 49, 252–260. ISSN 0946-672X.
- Pyatt, F.B., Grattan, J.P., 2001. Consequences of ancient mining activities on the health of ancient and modern human populations. J. Public Health Med. 23, 235–236.
- Ryan, P.C., Kim, J.J., Mango, H., Hattori, K., Thompson, A, 2013. Arsenic in a fractured slate aquifer system, New England, USA: influence of bedrock geochemistry, groundwater flow paths, redox and ion exchange. Appl. Geochem. 39, 181–192. https://doi.org/10.1016/j.apgeochem.2013.09.010.
- Santarelli, N., 2007. Le nickel: presqu'île de Kola et Nouvelle-Calédonie. Bulletin A.MI.S 51-52, 22 p.
- Simaa, M., Doldb, B., Frei, L., Senila, M., Balteanua, D., Zobrist, J., 2011. Sulfide Oxidation and Acid Mine Drainage Formation Within Two Active Tailings Impoundments in the Golden Quadrangle of the Apuseni Mountains. Romania.
- Smuda, J., Dold, B., Spangenberg, J.E., Pfeifer, H.R., 2008. Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: implications on sources and mobility of elements during transport and early stages of deposition. Chem. Geol 256 (1–2), 62–76.
- Smuda, J., 2009. Geochemical Evolution of Active Porphyry Copper Tailings impoundments: from Alkaline Deposition Towards acidification, PhD Thesis. University of Lausanne.
- Souza, E.S., Texeira, R.A., da Costa, H.S.C., Oliveira, F.J., Melo, L.C.A., do, Carmo, Freitas Faial, K., Fernandes, A.R., 2017. Assessment of risk to human health from simultaneous exposure to multiple contaminants in an artisanal gold mine in Serra Pelada, Pará, Brazil. Sci. Total Environ. 576, 683–695.
- Teng, Y., Wu, J., Lu, S., Wang, Y., Jiao, X., Song, L., 2014. Soil and soil environmental quality monitoring in China: a review. Environ. Int. 69, 177–199.
- Worlanyo, A.S., Jiangfeng, L., 2021. Evaluating the environmental and economic impact of mining for post-mined land restoration and land-use: a review. J. Environmental Manag. 279, 111623. https://doi.org/10.1016/j.jenvman.2020.111623.
- Yang, X., Zhao, H., Ho, P., 2017. Mining-induced displacement and resettlement in China: a study covering 27 villages in 6 provinces. Resour. Policy 53, 408–418.
- Youbi, N., Bellon, H., Marzin, A., Piqué, A., Cotten, J., Cabanis, B., 2001. Du cycle orogénique hercynien au pré-rifting de l'Atlantique central au Maroc occidental: les microdiorites des Jbilet sont-elles des marqueurs magmatiques de ce passage? Compt. Rend. Acad. Sciences-Series IIA-Earth Planet. Sci. 333 (5), 295–302.
- Zheng, Y., Ayotte, J.D., 2015. At the crossroads: hazard assessment and reduction of health risks from arsenic in private well waters of the northeastern United States and Atlantic Canada. Sci. Total Environ. 505, 1237–1247. https://doi.org/10.1016/j.
- Zouhri, L., El Amari, K., Marier, D., Benkaddour, A., Hibti, M., 2019. Bacteriological and geochemical features of the groundwater resources: kettara abandoned mine (Morocco). Environ. Pollut. 252, 1698–1708. Part BISSN 0269-7491.