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Environmental Contamination and Health Risk Assessment of Heavy Metals in the Stream Sediments of Oued Kasseb (Northerwest of Tunisia) in the Vicinity of Abandoned Pb–Zn Mine

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Abstract Mining activities have a positive impact on the global economy by increasing the socio-economic impact of the country's economic growth. However, they pose a high environmental risk of damaging sediments, and aquatic ecosystems by accumulating potentially toxic elements. Located in northern Tunisia, Oued Kasseb is one of the outlets of the Medjerda River, Tunisia's main watercourse and a major source of irrigation and drinking water. Oued Kasseb is the nearest watercourse to the Pb–Zn mining district of Djebel Hallouf-Sidi Bouaouane, a century-old mine (1890–1986). This study focuses on evaluating the spatial distribution of heavy metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)), their degree of contamination, using pollution indices, and on assessing the ecological and human health risks posed in the Oued Kasseb study area. The obtained heavy metal concentrations were in the following order: Pb > Zn > As > Cr > Ni > Cu > Cd. The spatial distribution shows that relatively high concentrations of metals were found in the vicinity of the Pb–Zn abandoned mine. The geoaccumulation index (I geo), the enrichment factor (EF), the contamination factor (CF), and the potential ecological risk index (RI) showed that the sediments are highly contaminated with As, Cd, Pb, and Zn, especially for sites surrounding the mine. The statistical analysis shows that As, Cd, Cu, and Pb are correlated strongly with Zn and appeared in the first component (F1:70.89%). The noncancerogenic risk revealed that As damages the children whereas it is not harmful to the adult group. The abandoned Pb–Zn mines are therefore the main source of heavy metals in the Oued Kasseb, causing serious environmental pollution and posing significant health risks.

Keywords Heavy metal · Mining area · Surface sediment · Spatial distribution · Pollution indices · Health risk

1 Introduction

Mining is one of the oldest and most important activities in the human being's history, with a major socio-economic impact (Candeias et al., 2018). However, themassive mining activities influence negatively the environment (Mobtaker & Osanloo, 2014). They represent the major anthropogenic source of potentially toxic chemicals that damage the aquatic ecosystems (Shul'kin et al., 2015), especially rivers and lakes which form the ecological barometer of a country's environmental health (Benjamin et al., 1996; Ben Ayed et al., 2022). In fact, mining harms the

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environment, in particular on sediments, water quality and, consequently, human health.

Abandoned mines pose high risks to human health and the environment through various discharges, including heavy metals in soils and sediments (Motswaiso et al., 2019). Heavy metals tend to settle on riverbeds or persist in streams or in soils for long periods, providing a long-term source of contamination for the surrounding inhabitants, as well as the hydrographic network and agricultural soils. These heavy metals can potentially harm the environment and human health because they continue to cause damage long after mining ceases. Consequently, the impact of mining on the aquatic environment has become a growing concern in recent decades (Younger & Wolkersdorfer, 2004) and the pollution of rivers by heavy metals has been a major research topic (Iordache et al., 2022).

Several studies have shown that the next 92% of heavy metals in aquatic ecosystems are associated with sediments but can easily migrate among waters and suspended matters through many geochemical reactions between the water–sediment interface (Ben Amor et al., 2019; Ayari et al., 2021; Hudson-Edwards et al., 2001; Meybeck & Helmer, 1989). This constitutes the essential problem especially since the waters of the rivers are vital sources of water ressources both for human consumption and for irrigation. Heavy metal pollution is also thoroughly investigated and its impacts on human health, the environment, and the ecosystem are determined (Yang et al., 2018; El-Zeiny & Abd El-Hamid, 2022).

Northern Tunisia is one of the most significant lead districts in Africa (Boussen et al., 2010). It contains several types of mines (lead, zinc, fluorine, etc.) in the northwestern region (Sainfeld, 1952; Slim-Shimi, 1992; Bouhlel, 1993; Mezned et al., 2008), especially around Medjerda River, the country's main watercourse. In addition, in Tunisia, the Medjerda basin is one of the most important agricultural sectors (Guellala et al., 2012). In fact, the needs for irrigation water are important, therefore during the rainy season, the Medjerda River and its tributaries are the main sources for irrigation. In this area, approximately 2.3 million tonnes of lead, 2.0 tonnes of zinc, and 0.8 tonnes of fluorite are extracted and processed (Boussen et al., 2010). Since the beginning of the mining activity in 1910, the Jebel Hallouf deposit (exploited by a mining company between 1965 and 1986) has produced nearly 326.541 tonnes of lead and 14.207 tonnes of zinc (Ben Hassene, 2006; Jemmali et al., 2013).

No data are published on the Oued Kasseb basin (Fig. 1) tributary of the Medjerda River. The main objectives of this study are to (1) assess the spatial distribution of heavy metals in stream sediment, (2) to investigate the degree of contamination by As, Cd, Cr, Co, Ni, Pb, and Zn and the potential ecological risk, (3) to estimate the associated level of health risks for adults and children exposed to contaminated soil and sediments. The results of this study will be useful for understanding soil and sediment contamination in the area of the abandoned Pb–Zn mine especially in Oued Kasseb, the effluent of Medjerda River, and the risk to human health. This work can serve as a basis for data for human health risk assessment and the environment around the abandoned mine in Tunisia.

2 Study Area

Oued Kasseb is an affluent of Oued Medjerda. It is mostly used for human water consumption and in agriculture (Fig. 1). This river, the nearest watercourse to the Djebel mine Hallouf-Sidi Bouaouane, is located in northern Tunisia, 10 km north of Bou Salem and more than 140 km west of Tunis. It is the watercourse on which a dam was built near the mining area in 1985. It drains a 255 km^2 basin, 101 km^2 of which is controlled by the Kasseb Dam dedicated for drinking water. Its catchment area is made up of allochtone flysch as well as autochthonous marl and marl-limestone. The Djebel Hallouf-Sidi Bouaouane mining area is located 10 km north of Bou Salem in the northwestern part of Tunisia and more than 140 km west of the capital of Tunisia (Chakroun et al., 2006). This district's mining wastes are kept on the mining site located in the catchment of Oued Kasseb. The mining district of Jebel Hallouf-Sidi Bou Aouane is divided into two primaries (Chakroun et al., 2006; Mansouri, 1987; Sainfeld, 1952): that connected to the post-napped neogene strata, neogene conglomeratesand Sidi Bou Aouane's eocene substratum, and that associated to Jebel Hallouf's filonienne and karstic mining in the campanien calcaires (Chakroun et al., 2006). Jebel Hallouf and Sidi Bou Aouane deposits, known as

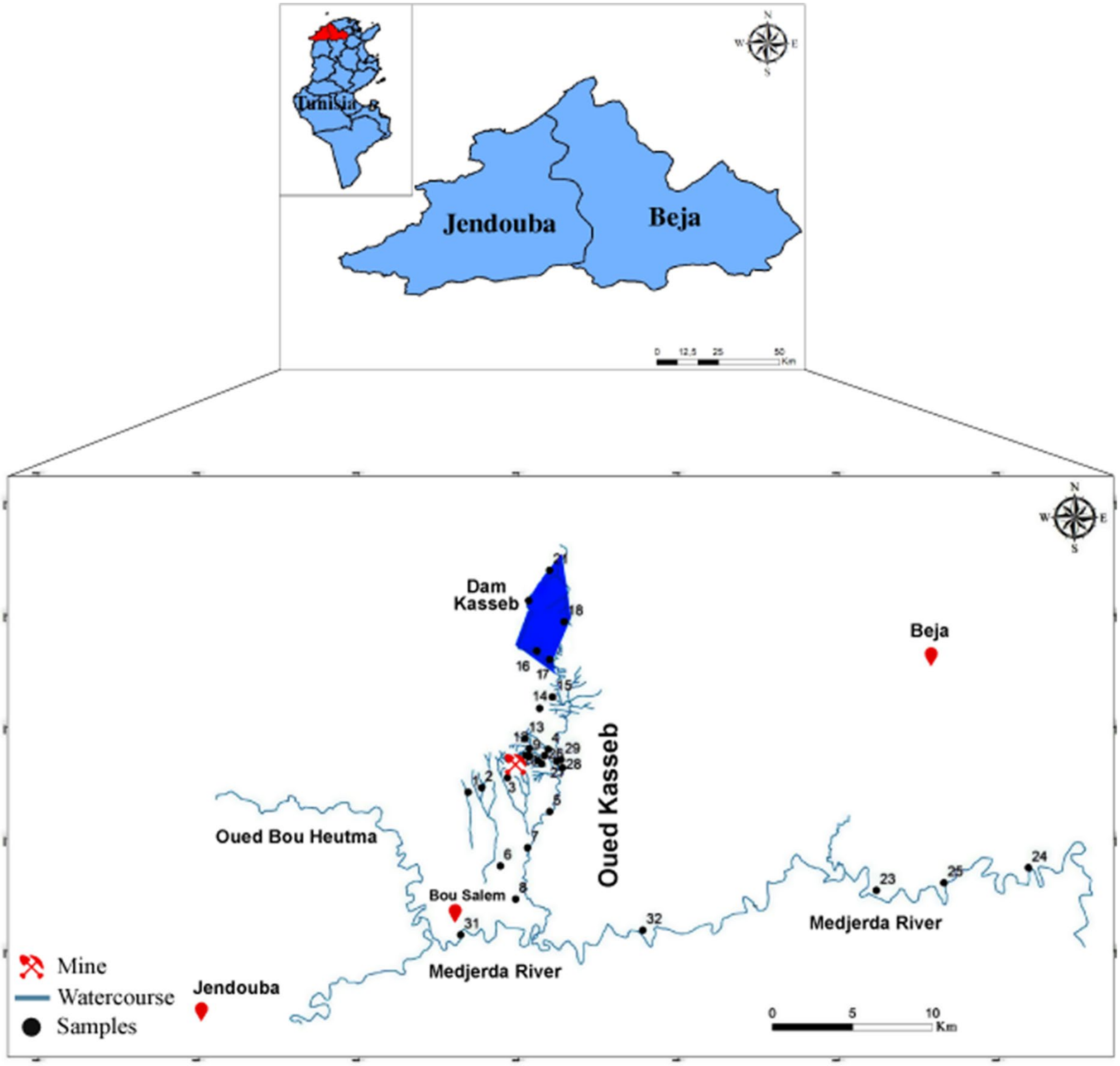


Fig. 1 Study area of surface sediments in Oued Kasseb catchment

the Jebel Hallouf deposit, are located in the Nappe Zone's exterior zone, 17 km west of Beja (Jemmali et al., 2013). The former, with sub-horizontal Neogene continental layers covering the whole area, is an E-W anticline surrounded by Eocene strata (Chakroun et al., 2006). However, the second is situated near the periclinal side of Jebel Hallouf anticline on the margins of a trough-shaped Neogene syncline that stretches in a SW-NE direction (Chakroun et al., 2006; Mansouri, 1980).

3 Materials and Methods

The sampling location distribution is shown in Fig. 1. A surface sediment sampling campaign was carried out in October 2019. 32 samples, distributed around the entire Oued Kasseb catchment in the Jendouba (Bou Salem) governorate in northern Tunisia, were analyzed for metal trace elements (As, Cd, Cr, Co, Ni, Pb, Zn). The analysis was performed on sediments containing fractions below or equal to 180 µm by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the National Office of Mines.

Samples were collected using a stainless-steel shovel; each of which was placed in a plastic bag and stored at 4 °C to be analyzed chemically. In the laboratory, surface sediments are used for trace metal analysis by the plasma torch method. Then, sediments were oven-dried at 40 °C. In order to obtain a sample with a homogeneous composition, the sample is crushed in a divider. The samples were disc-crushed to obtain fine sediments with a diameter of 0.1 mm.

To analyze the trace metal analysis, 0.5 g of dried and crushed sediment was placed in Teflon and digested by adding hydrofluoric acid (20 mL), perchloric acid (5 mL), and nitric acid (2 mL). Then, it was heated at 125 °C using a hot plate and allowed to evaporate until becoming completely dry. After the mineralization of the sediments, the samples were recovered by adding 10 mL of HCL (37%), and the solution was put in a 50 ml flask. After cooling, the volume of the solution was adjusted to the gauge mark.

In order to validate the accuracy of the metal concentration, the dosages were estimated by repeating the analysis. Each obtained concentration value is the average of three replicates. The samples and blanks were analyzed at the same conditions using the same method and similar reagent volume. Standard solutions were used to determine all metal concentrations. Measurement error precision was estimated to be ± 5% for all analyzed metal results.

3.1 Environmental Risk Assessment

To assess the degree of contamination in the surface sediments of the Oued Kasseb catchment, the geo-accumulation index (Igeo), the contamination factor (CF), and the enrichment factor (EF) were determined. The classification of the pollution indicators is presented in Table 1.

The geo-accumulation index (Igeo) was specified according to the following equation (Muller, 1969):

$$I_{geo} = \log_2\left(\frac{C_m}{1.5C_B}\right)$$

where C_m is the concentration of the element in the sediment sample and C_B denotes the geochemical background concentration of the metal (the UCC). The value 1.5 is the background matrix correction factor used to characterize the rock geology, sedimentary characteristics as well as certain anthropogenic factors (Yan et al., 2020).

According to Zoller et al. (1974), the enrichment factor (EF) was calculated as follows:

Table 1 Classification of Environmental risk index

Index	Risk classification
Geoaccumulation index (Igeo)	Igeo ≤ 0 uncontaminated
	0 < Igeo ≤ 1 uncontaminated to moderately contaminated
	1 < Igeo ≤ 2 moderately contaminated
	2 < Igeo ≤ 3 moderately to strongly contaminated
	3 < Igeo ≤ 4 strongly contaminated
	4 < Igeo ≤ 5 strongly to extremely contaminated
	Igeo > 5 extremely contaminated
Enrichment factor (EF)	EF < 1 no enrichment
	1 < EF < 2 minor enrichment
	2 < EF < 5 moderate enrichment
	5 < EF < 20 significant enrichment
	20 < EF < 40 very high enrichment
	EF > 40 extremely high enrichment
Contamination factor (CF)	CF < 1 low contamination
	1 < CF < 3 moderate contamination
	3 < CF < 6 considerable contamination
	6 > CF very high contamination

$$EF = \frac{\left({}^{C_m}/{}_{C_{Zr}}\right)\mathrm{Sample}}{\left({}^{C_m}/{}_{C_{Zr}}\right)\mathrm{Background}}$$

where the Zircon (Zr) is a natural element of reference while the (C_m/C_{Zr}) Sample and (C_m/C_{Zr}) Background are the concentration ratios of the metal m and the reference Zr in the sample and background, respectively.

According to Hakanson (1980), the factor of contamination (CF) can be calculated using the formula written below:

$$CF = \frac{C_m}{C_B}$$

where C_m is the metal concentration in the sediment sample and C_B corresponds to the geochemical background of the metal.

3.2 Ecological Risk Assessment

The risk index (RI) and the ecological risk index (Er) were utilized to assess the potential impact of pollutants on the environment.

The Potential Ecological Risk Index, which takes into account the metal content of the sediments, is generally employed to evaluate heavy metal pollution (Luo & Jia, 2021). It shows the relationship between the ecological and environmental effects of heavy metals and toxicology, allowing a more accurate representation of the impact of heavy metals on the ecological system (Pelfrêne et al., 2013; Luo & Jia, 2021). The classification of the potential ecological risk index is shown in Table 2.

The risk indexes were calculated using the following formulae:

$$E^i_r = T^i_r \times CF^i$$

$$RI = \sum_{i=1}^{n} E^i_r$$

where E^i_r is the potential ecological risk index of an individual metal; CF^i designates the contamination factor of each heavy metal; T^i_r represents the toxic response coefficient of heavy metal i (As = 10, Cd = 30, Cr = 2, Cu = 5, Ni = 5, Pb = 5, and Zn = 1) and RI refers to the potential ecological hazard index of all heavy metals in the surface sediments.

3.3 Statistical Analysis

The statistical analysis was performed using XLSTAT (2022) to determine the relation between trace metals. The correlation matrix, the Principle Component Analysis (PCA), and the Hierarchical Cluster Analysis HCA were applied to analyze the data of 32 samples of the study area.

In the conducted experiments, Pearson correlation analysis was performed to determine the relationship between heavy metals and the studied samples. The correlation between metals may indicate if they were all derived from the same or different sources.

The Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were conducted to provide information on the sources and pathways of heavy metals (Hu et al., 2013).

3.4 Human Health Risk Assessment

The Health Risk (HR) index assessment was carried out to calculate the human carcinogenic and non-carcinogenic risks resulting from ingestion, inhalation, and dermal contact of the surface sediments of the Oued Kasseb catchment (Table 3 and 4).

The relationship between the human health and heavy metals concentrations can be assessed using the

Table 2 Classification of potential ecological risk index

E^i_r	Risk classification	RI	Risk classification
$E^i_r < 40$	Low risk	RI < 150	Low risk
$40 < E^i_r < 80$	Moderate risk	150 < RI < 300	Moderate risk
$80 < E^i_r < 160$	Considerable risk	300 < RI < 600	Considerable risk
$160 < E^i_r < 320$	High risk	RI > 600	High risk
$E^i_r > 320$	Significantly high risk		

Table 3 Parameters of the equations for the assessment exposure health risks of heavy metals

Exposure parameters		Units	Child	Adults
IngR [a]	Ingestion rate	mg/day	200	100
InhR [a]	Inhalation rate	m^3/day	7.63	12.8
ED [b]	Exposure duration	Year	6	24
AT [c]	Average time	days	ED*365	ED*365
SA [b]	Exposed skin area	cm^3	1600	4350
PEF[b]	Emission factor	m3/kg	1.36E+09	1.36E+09
AF [b]	Adherence factor	mg/cm^2-day	0,2	0,7
BW [d]	Body weight	kg	15	70
EF [e]	Exposure frequency	days/year	350	350
ABS [a]	Dermal absorption factor	Unitless	0,001	0,001

[a] USEPA, 2001;Ghouma et al., 2022

[b] USEPA, 2001; Adimalla et Wang, 2018

[c] USEPA, 1989;Ghouma et al., 2022

[d] Narsimha & Rajitha, 2018; Adimalla et Wang 2018

[e] Qing et al., 2015;Ghouma et al., 2022

Table 4 Summary of reference doses (RfD) of heavy metals

	ingestion	inhalation	dermal
As*	0.0003	0.000123	0.000123
Cd**	0.001	0.00001	0.0005
Cr*	0.003	0.0000286	0.00006
Cu*	0.04	0.04	0.012
Ni*	0.02	0.0206	0.0054
Pb*	0.0035	0.00352	0.000525
Zn*	0.3	0.3	0.06

*USEPA 2001, 1997; Adimalla et Wang, 2018

**Barraza et al., 2018; Ghouma et al., 2022

Health Risk Hazard method introduced by the United States Environmental Protection Agency (USEPA) guidelines (Li et al., 2020). The degree of health risk varies from one region to another and is influenced by the duration of exposure to trace metals, the amount of tolerance, the lifestyle, body weight, and the individual's daily habits (Kumar et al., 2020).

Three routes of exposure (ingestion, dermal, and inhalation) were considered in the performed experiments (Li et al., 2020). The average daily metal intake (ADI) from the contaminated sediments was calculated using the following equations:

$$\mathrm{ADI}_{\mathrm{ingestion}} \frac{C_{\mathrm{sed}} \times \mathrm{IngR} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6}$$

$$\mathrm{ADI}_{\mathrm{inhalation}} \frac{C_{\mathrm{sed}} \times \mathrm{InhR} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}}$$

$$\mathrm{ADI}_{\mathrm{dermal}} \frac{C_{\mathrm{sed}} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6}$$

where $\mathrm{ADI}_{\mathrm{ingestion}}$ refers to the average daily intake by ingestion; $\mathrm{ADI}_{\mathrm{inhalation}}$ designates the average daily intake of inhalation; $\mathrm{ADI}_{\mathrm{dermal}}$ is the average daily intake through the skin (mg/kg/day); C_{sed} represents the measured pollutant concentration (mg/kg); IngR and Inh are the rates of ingestion (mg/d) and inhalation (m^3/d) respectively; EF corresponds to the exposure frequency (day/year); ED denotes the exposure duration (year); BW is the body weight (kg) of the exposed person; AT refers to the average dose time (day); SA denotes the exposed skin surface area (cm^2); AF represents the adherence factor (kg/cm^2-day); ABS is the dermal absorption factor and PEF designates the emission factor (m^3/kg) (Li et al., 2020).

The non-carcinogenic risks caused by the different pathways of heavy metals in sediments can be assessed using the target hazard ratios (HQ) considered to evaluate the levels of toxicity (Varol et al., 2020). The HQ was calculated using the formula written below:

$$HQ = \frac{ADI}{RfD}$$

The hazard index (HI) was employed to assess the risk of carcinogenic health effects caused by heavy metals. The (HI) was determined by summing the HQs of heavy metals. It was calculated using the following formula:

$$HI = \sum HQ = \sum \frac{ADI}{RFD}$$

where RFD corresponds to the reference dose mg/kg day. when $HI < 1$, there is no noncarcinogenic health risk; whereas when $HI > 1$, a potential noncarcinogenic health risk is observed (Luo & Jia, 2021).

The carcinogenic risk (CR) and the total carcinogenic risk (TCR) are indices indicating the health risk caused by heavy metals (Luo & Jia, 2021). They measure the probability of lifetime cancer risk for a human who has been exposed to a carcinogenic metal (Li et al., 2014).

$$CR = \sum ADI \times SF$$

$$TCR = \sum CR$$

The slope factor (SF) of ingestion ((mg/kg)/day) is: 1.5 As, 3.8 10^{-1} for Cd, 5 10^{-1} for Cr, 8.5 10^{-3} for Pb, and 9.1 10^{-1} for Ni. The SF of dermal ((mg/kg)/day) is 3.66 for As, 1.58 10^{-1} for Cd, 2.1 for the Cr, 4.55 for Ni, and 4.25 10^{-1} for Pb. Concerning inhalation, the SF ((mg/kg)/day) is 1.5 10^{1} for As, 6.30 for Cd, 4.1 10^{1} for Cr, 8.4 10^{-1} for Ni, and 4.2 10^{-2} for Pb (Barraza et al., 2018; Ghouma et al., 2022).

4 Results and Discussion

4.1 Spatial Distribution of Heavy Metal Concentrations

The results of heavy metals concentration in the Oued Kasseb study area are presented in Fig. 2 and Table 5.

The mean, minimal, and maximum metal concentrations in the Oued Kasseb catchment of the surface sediment and the Upper Continental Crust (UCC) values are shown in Table 5.

The obtained total concentrations of trace metals in the surface sediments range from 0.5 to 1300 mg/kg for As with an average of 167.3, from 1 mg/kg to 58.7 mg/kg for Cd with an average of 12.3, from 26.6 mg/kg to 130.9 mg/kg for Cr with an average of 72.4, from 9.7 mg/kg to 102.5 mg/kg for Cu with an average of 29.3, from 13.9 mg/kg to 46.3 mg/kg for the Ni with an average of 31.1, from 10.5 mg/kg to 23,900 mg/kg for Pb with an average of 3061.4, and from 35.5 mg/kg to 8924.3 mg/kg for Zn with an average of 2031.3. The results of the trace metal contents reveal that heavy metal concentrations can be presented in the following order: Pb > Zn > As > Cr > Ni > Cu > Cd.

Arsenic The As concentrations in the Oued Kasseb watershed's surface sediments range from 0.5 mg/kg to 1300 mg/kg. Upstream concentrations of the arsenic are lower than that of UCC values which is around 1.5 mg/kg (Taylor & McLennan, 1985). The highest concentrations, ranging from 103 mg/kg to 1300 mg/kg, were found near the mine area. These concentrations decrease going downstream. It is also obvious that As concentrations in the surface sediments from the Medjerda River are lower than the UCC value. Median As value was 167.3 mg/kg, far superior to those found in contaminated mining sites. In general, arsenic occurs naturally in the earth's crust (Dowdle et al., 1996; Gorny et al., 2015). This metal has increased in many continental water systems as a result of anthropogenic activities such as mining, copper smelting, disposing of waste, use of some herbicides and pesticides, feeding animals, and fossil fuel burning… (Santelli et al., 2001; Drahota et al., 2009; Gorny et al., 2015).

Cadmium The values of Cd in the Oued Kasseb study area range from 1 mg/kg to 58.7 mg/kg. The surface sediment concentrations indicate that the upstream concentrations are higher than the UCC value of around 0.1 mg/kg (Taylor & McLennan, 1985). The highest concentrations of Cd, ranging from 2.5 mg/kg to 58.7 mg/kg, were found near the mine meaning that Cd concentrations were mostly related to mineral occurrences and mining wastes. The concentrations in Medjerda River range between 1 mg/kg and 1.1 mg/kg, with values higher than the UCC but less significant than those measured in Oued Kasseb.

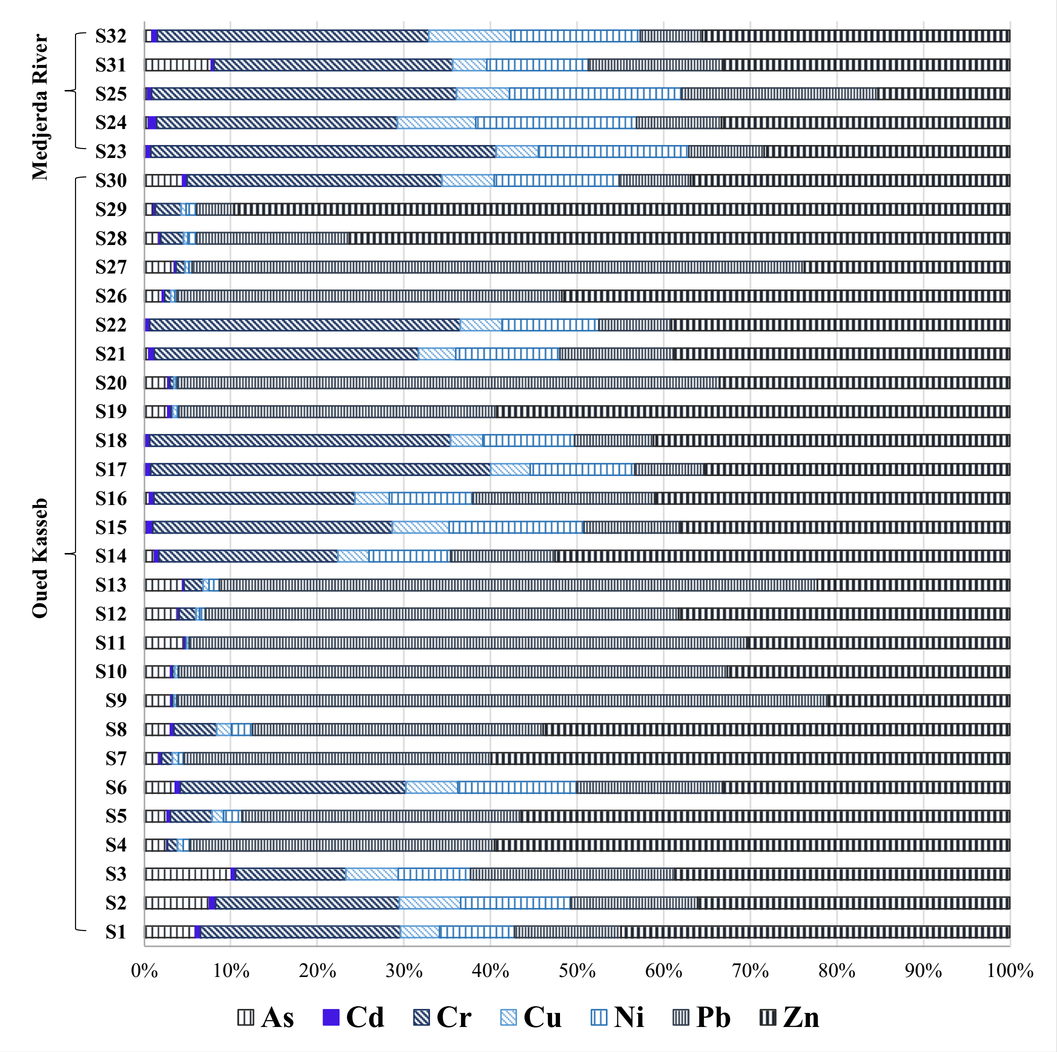


Fig. 2 Heavy metals distribution in surface sediment from the Oued Kasseb catchment

Table 5 Minimum, maximum, and mean of heavy metal concentrations in mg/kg from Oued Kasseb surface sediments

		As	Cd	Cr	Cu	Ni	Pb	Zn
Oued Kasseb	Min	0.5	1.3	26.6	11.7	13.9	20.8	74.5
	Max	1300	58.7	130.9	102.5	40.8	23,900	8924.3
	Mean	197.2	14.3	73.3	32.4	30.7	3623	2396.5
Medjerda River	Min	0.5	1	29.8	9.7	19.9	10.5	35.5
	Max	25.4	1.1	90.5	15.3	46.3	52.9	108.9
	Mean	5.7	1	67.8	12.6	33.3	29	59.7
Study area	Min	**0.5**	**1**	**26.6**	**9.7**	**13. 9**	**10.5**	**35.5**
	Max	**1300**	**58.7**	**130.9**	**102.5**	**46.3**	**23,900**	**8924.3**
	Mean	**167.3**	**12.3**	**72.4**	**29.3**	**31.1**	**3061.4**	**2031.3**
	UCC	**1.5**	**0.1**	**35**	**25**	**20**	**17**	**71**

UCC: Concentrations in ppm of the Upper Continental Crust (Taylor et McLennan, 1985)

Chromium The surface sediment concentrations in Oued Kasseb watershed range between 26.6 mg/kg and 130.9 mg/kg. The Cr values show that the highest concentrations were measured at the upstream of Oued Kasseb at the dam, with values ranging from 82.7 mg/kg to 130.9 mg/kg. These values are extremely high, compared to the UCC values (Cr:35 mg/kg) (Taylor & McLennan, 1985). It is also clear that the gradient decrease from upstream of the Kasseb dam to downstream as the concentration of Cr gradually declines from 118.3 mg/kg to 26.6 mg/kg.

Copper The Cu amounts in Oued Kasseb watershed's surface sediments range from 9.7 mg/kg to 102.5 mg/kg. The concentration of Cu is below the UCC value of around 25 ppm in the upstream section of Oued Kasseb (Taylor & McLennan, 1985). However, the highest concentrations, ranging from 15.9 mg/kg to 102.5 mg/kg, were found near the mine. These concentrations decrease going downstream. Cu concentrations in the studied samples vary between 9.7 mg/kg and 15.3 mg/kg at the Medjerda River level. They are lower than the UCC value.

Nickel The Ni content in the Oued Kasseb surface sediments ranges from 13.9 mg/kg to 46.3 mg/kg. The contents of Ni from the Kasseb dam and the watercourse are from 13.9 to 40.8 mg/kg. These concentrations are higher than those in UCC which are around 20 mg/kg (Taylor & McLennan, 1985). This finding suggests that the nickel came from mine tailings and dykes. The Ni concentrations in Medjerda River samples range from 19.9 mg/kg to 46.3 mg/kg. These values are well above that of UCC.

Lead The content of Pb in Oued Kasseb watershed's surface sediments varies between 10.5 mg/kg and 23,900 mg/kg. Lower concentrations were measured at the dam level and, thus, at the upstream of Oued Kasseb. Most of the Pb concentrations in the surface sediments collected from the Medjerda River exceed the UCC values. It is obvious that the Pb concentration, corresponding to 17 mg/kg, is higher than the UCC value throughout Oued Kasseb, (Taylor & McLennan, 1985). This distribution results from the lead and zinc emissions from Djebel Hallouf-Sidi Bouaouane mine.

Zinc The concentrations of Zn in Oued Kasseb study area vary between 35.5 mg/kg and 8924 mg/kg. The highest concentrations were found near the mine. Although Zinc values gradually decline at the downstream of Oued Kasseb (far from the mine), they remain high. In general, throughout Oued Kasseb, the Zn concentrations are higher than the UCC value which is equal to 71 mg/kg (Taylor & McLennan, 1985). This distribution can be explained by lead–zinc discharges from the mine and dyke at Djebel Hallouf-Sidi Bouaouane. On the other hand, concentrations in Zinc around Medjerda River are low. They range between 35.5 mg/kg and 61.3 mg/kg, except for S31 where the Zn concentration in Medjerda River samples is lower than the UCC value.

The mean values of the seven heavy metals (As, Cd, Cr, Ni, Pb, and Zn) values are higher than the Concentrations of the Upper Continental Crust (Taylor & McLennan, 1985). In fact, the average concentrations are typically higher than the UCC value used as a reference (Taylor & McLennan, 1985), except for copper and zinc around Medjerda River where concentrations are lower than the UCC. Overall, high levels of trace metals were identified in the area surrounding the old mining region located in oued Kasseb catchlment. However, the surface sediments in Medjerda River study area have mostly low concentrations.

The spatial distribution of the metals shows that the surface sediments collected in the vicinity of the abandoned mine have the highest levels of heavy metals. In fact, the concentrations of the As, Cd, Cu, Pb, and Zn, at sites around the abandoned mine area (S7, S9, S10, S11, S19, S20, S26, and S27) were much higher than at the Kasseb dam, far from the mining area, and in the Medjerda River. The contents of these metals were found to be high in the area of the abandoned Pb–Zn mine and gradually decreased with the distance from the vicinity. These results indicate that the stations around the mine are highly contamined, which shows that the study area is exposed to high contamination risk. Such mining wastes may represent a source of heavy metals near mine sites. In fact, the contents of heavy metals vary according to the distance from the source of pollution as well as the nature and behaviour of the metals discharged from the tailings and mining wastes (Mlayah et al., 2005, 2017).

The high concentrations in the surface sediments are, therefore, caused by anthropogenic sources, in particular by old mining operations. They can also result from the discharges from the town of Bousalem and the use of pesticides on the adjacent farmland. Indeed, the high levels of heavy metals, especially arsenic, are not only due to mining and other human activities, but also to natural sources in the region's soil (Jdid et al., 1999). In addition, other factors, such as erosion, run-off and the prevailing southwesterly winds as well as the changes in the adjacent land, may also affect the spatial distribution of the trace metals in Oued Kasseb catchment. These toxic pollutants can be discharged into Oued Kasseb, the agricultural areas and Medjerda River used for irrigation and human consumption. Heavy metals released from Pb–Zn mines can be activated, transported, and accumulated in various targets and they can have direct or indirect effects on plants, animals, and human beings (Wang et al. 1994; Chiaradia et al. 1997; Grattan et al. 2002; Liu et al. 2005a, b; Pusapukdepob et al. 2007; Bai and Yan 2008; Kim et al. 2008; Zhang et al., 2012).

4.2 Comparison of Heavy Metals Concentrations in the Surface Sediments of Oued Kasseb with those in other Worldwide Localities:

In order to compare the heavy metal concentrations in the surface sediments of Oued Kasseb catcment with those in worldwide localities, heavy metal concentrations in northeastern Tunisia, Algeria, Morocco, Spain and Greece were collected around the mining-affected areas (Table 6).

The comparision of the different study area proves that the sediment samples taken from Oued Kasseb catchment show high levels of heavy metals.

Compared to other areas, the examined surface sediments in Oued Kasseb watershed contain very high levels of heavy metal polluted sediments, mainly As, Cd, Pband Zn. Therefore, considering the following heavy metals (As, Cd, Cr, Cu and Ni), the concentrations in the sediments from Spain are higher than those of the sediments from NE Tunisia, Algeria, Morocco and Greece regions. In terms of Zn concentrations, Algeria and NE-Tunisia have higher values than the examined sediments in other study areas, but lower values than Oued Kasseb catchment. The Pb concentrations in the sediments located in Morocco are lower than those of the sediments in Oued Kasseb catchment, but higher than those recorded in other study areas.

The comparative study indicates that high concentration of metals in the sediments is generally due to the heavy metal pollution caused by the mining activities. As a result, the comparison of the different study regions emphasizes the importance of the metal contamination in the surface sediments from Oued Kasseb catchment.

4.3 Statistical Analysis

Statistical analysis was performed to assess the general distribution of heavy metals contamination in Oued Kasseb catchment study area.

Table 6 Comparison of heavy metal concentrations (mg/kg) in the Oued Kasseb catchment with other studies area

Localisation	As	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Oued Kasseb	0.5 -1300	1—58.7	26.6—130.9	9.7—102.5	13.9—46.3	10.5—23,900	35.5—8924.3	This study
Tessa River, NW Tunisia	NA	1–5	39—90	8–50	16—89	17—356	100—2500	Sebei et al. 2018
Algeria	NA	7.8—28.8	11.4—20.22	16.8—47.2	4.5—64.2	235.6—871.2	2009—3411.2	Khelfaoui et al., 2020a, 2020b
Morocco	104.6—289	0.1—0.5	28.8—125	8.9—22.9	2—21	43.8—9889.3	40.8—121.8	Nassiri et al., 2021a, 2021b
Spain	190 – 596	5—50	b.d.l—158	70—265	1—188	10.06—691	12.23—1972	González-Corrochano et al., 2014
Greece	7.5—24.6	0.7—34.7	NA	14.9—130.7	NA	39.7—302	1.99—178.7	Nikolaidis et al., 2010a, 2010b

*NA: not availbale

*b.d.l: below the detection limit

4.3.1 *Matrix Correlation*

To examine the relationships between heavy metals in the surface sediments of Oued Kasseb catchment, a Pearson correlation matrix with P significance (<0.05) was utilized.

Table 7 shows the strongly positive correlations between heavy metals (As, Cd, Cu, Pb and Zn ($p<0.05$) in the surface sediments of Oued Kasseb catchment. In fact, the positive correlations between As ($r=0.84$), Cd ($r=0.97$), Cu ($r=0.95$) and Pb ($r=0.841$) with Zn indicate a similar geochemical and/or a common origin. The correlation between Pb–Zn ($n=0.81$) can be explained by lead–zinc discharges from Djebel Hallouf-Sidi Bouaouane mine. The elements with significant correlation have similar behaviour under the same environmental conditions, probably due to the anthropogenic sources from the abondoned Pb–Zn urban inputs, the pesticide and mine use in farms. Moreover, the correlations between heavy metals show that these elements can be originate from common pollutant discharge sources and have the same dependencies during transport and remobilization in the riverine sediments (Iordache et al., 2022; Mirzabeygi et al., 2017).

4.3.2 *Principal Component Analysis (PCA)*

The Principal Component Analysis (PCA) demonstrated that the surface sediments of Oued Kasseb catchment originate from two distinct sources. It also showed that seven heavy metals in the surface sediments of Oued Kasseb catchment can be described using two principal components (F1 (70.89%) and F2 (21.17%)) which accumulate 92.15% of the total variance (Fig. 3).

The variable space F1 that explains 70.89% of the variance, defined by a positive charge of the contents of As, Cd, Cu, Pb and Zn. The significant correlations between these metals in the main component F1 prove that these metals have an anthropogenic origin, principally from the old mining operations, the discharges from the urbanized areas and the pesticide use in the adjacent farmland. F2, presenting 21.17% of the variance, is characterized by the positive contributions of Cr and Ni. These metals are of natural origin and have been affected by erosion, water runoff, and other factors such as the alteration of the adjacent land.

4.3.3 *Hierarchical Cluster Analysis (HCA)*

The Hierarchical Cluster Analysis (HCA) was applied to a surface sediment sample quality in order to assess metal variables and demonstrate spatial sampling strategies (Zhao et al., 2015). Surface sediments were clustered hierarchically to predict the sites similarity based on their proximity. The degree of association between the variable groups is represented by the distance axis. In other words, the lower the value on the axis is, the stronger the association will be (Hu et al., 2013).

The HCA was used to determine the groups of similar sampling sites of the surface sediments of Oued Kasseb catchment. These sites were classified into two groups according to the concentration of heavy metals in the surface sediments of Oued Kasseb catchment (Fig. 4).

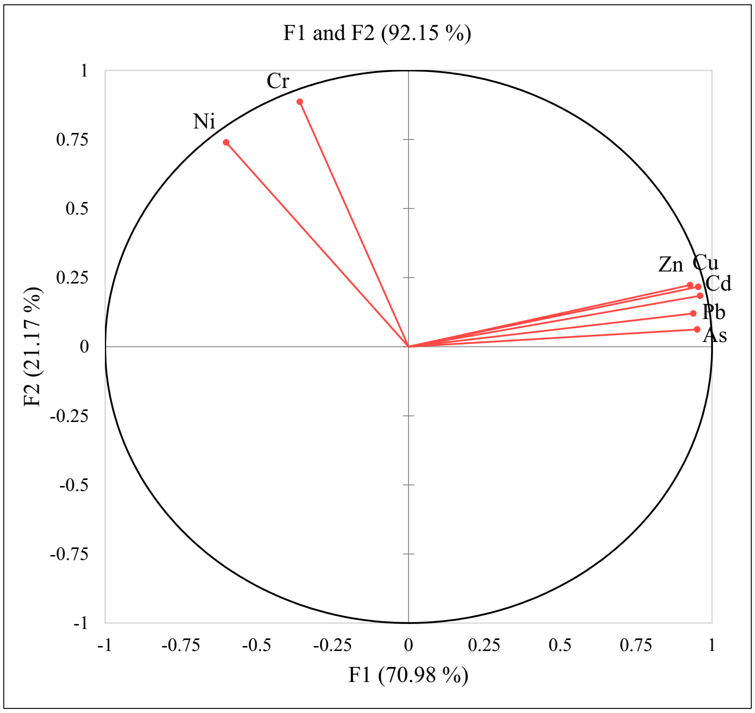
The first group (G-1) includes sites near and around the mining area where the highest heavy metal concentrations were observed. The samples from G-1 showed that the site is located in a highly- polluted area receiving contaminated discharges released from the abondonet Pb–Zn mine.

Two subgroups were identified in the second group (G-2). They form one group (G2-1) in

Table 7 Matrix correlation (Pearson (n)) of heavy metals contents in the sediments of Oued Kasseb catchment

	As	Cd	Cr	Cu	Ni	Pb	Zn
As	**1**	**0.88**	-0.26	**0.88**	-0.53	**0.96**	**0.84**
Cd		**1**	-0.21	**0.97**	-0.43	**0.87**	**0.97**
Cr			**1**	-0.18	**0.79**	-0.19	-0.17
Cu				**1**	-0.40	**0.89**	**0.95**
Ni					**1**	-0.50	-0.37
Pb						**1**	**0.81**
Zn							**1**

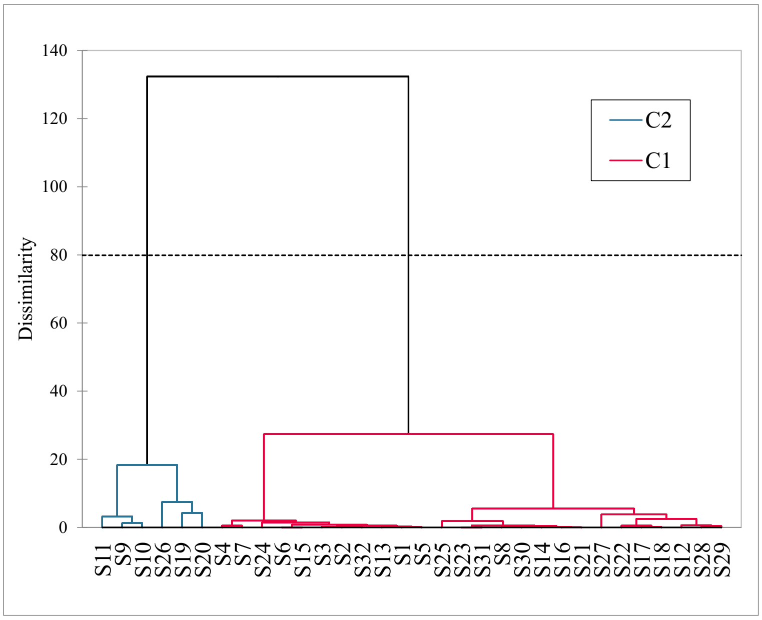
Fig. 3 Principal component loading of heavy metal variables



moderately- contaminated areas and one group (G2-2) in relatively low contaminated area. Indeed, the first sub-group (G 2–1) includes sites with higher heavy metal concentrations than those in sub-group (2–2) located in Oued Kasseb far away from the mine. However, sub-group (G 2–2) contains samples from Medjerda River and Oued Kasseb upstream.

The HCA classification was conducted according to the quality of the surface sediment samples of Oued Kasseb catchment and their proximity to the

Fig. 4 Hierarchical cluster analysis (HCA) dendrogram of heavy metal content of surface sediment sampling areas



source of pollution which was predominantly mining discharges.

The correlation between heavy metals is used to classify different groups of chemical elements with different or similar geochemical behavior (Resongles et al., 2014). The As, Cd, Cu, Pb, and Zn were closely correlated with each other and appeared in the first component, suggesting a common source of these elements (Al-Hobaib et al., 2013; Gong et al., 2014). This significant correlation indicates that these metals have an anthropogenic origin, mainly from old mining activities, discharges from urbanised areas, and the use of pesticides on adjacent agricultural land. The distribution of Cr and Ni and their relationship to the station show that the metals are of natural origin and have been influenced by erosion, water run-off, and other factors such as adjacent land alteration. The classification of clusters shows the distances between the surface sediment samples, suggesting the existence of two main groups with a similar origin or level of contamination. In general, the statistical analysis suggests a common origin for these elements. This is also related to their level of contamination.

4.4 Assessment of Heavy Metal Contamination

4.4.1 Geo-Accumulation Index

The geo-accumulation index (Igeo) was used to compare the contamination of the different trace metals in the studied sediments using a background geochemical reference (UCC). The Igeo values were calculated employing the trace metal concentrations to assess the level of pollution in the surface sediments of Oued Kasseb catchment. The Igeo values for the selected trace metals (As, Cd, Cr, Cu, Ni, Pb and Zn) are shown in Table 8.

The latter demonstrates that the geo-accumulation index (Igeo) values range from -2.17 to 9.17 for As; from 2.74 to 8.61 for Cd; from -0.98 to 1.32 for Cr; from -1.95 to 1.45 for Cu; from -1.11 0.63 for Ni; from -1.28 to 9.87 for Pb and from -1.58 to 6.39 for Zn. Igeo mean values in the examined surface sediments decline in the following order: Pb (4.78) > Cd (3.31) > As (3.05) > Zn (2.12) > Cr (0.35) > Ni (0.01) > Cu (-0.78).

The geoaccumulation index calculation results reveal that Cr, Cu and Ni represent unpolluted to moderately-polluted sediments. The Igeo values in the surface sediments of Oued Kasseb catchment show no to extreme contamination of As, Cd, Pb and Zn. With the exception of Cr, Cu and Ni, the heavy metals As, Cd, Pb and Zn have values higher than 5. This indicates an extreme level of contamination. The distribution of Igeo accumulation Index proves that the study area is heavily polluted by As, Cd, Pb and Zn, mainly in and around the old mine and at the downstream of Oued Kasseb.

4.4.2 Enrichment Factor

The enrichment factor of each metal was determined in order to evaluate the anthropogenic influences on the trace metals in Oued Kasseb catchment sediments. The obtained results are presented in Table 8.

The latter demonstrates that the enrichment factor (EF) values vary from 1.1 to 15,987.1 for As; from 41.9 to 10,035 for Cd; from 4.4 to 19.7 for Cr; from 1.6 to 59.1 for Cu; from 4.6 to 18.5 for Ni; from 3.3 to 19,857.2 for Pb and from 2.7 to 2242.2 for Zn. It also shows that the mean values of the EF in the studied surface sediments decrease in the following order: Pb (1754.1) > Cd (1149.5) > As (1143.1) > Zn (256.7) > Cr (10.1) > Cu (8.9) > Ni (7.8).

The values of the enrichment factor reveal a low enrichment ($EF<2$) to extremely high enrichment ($EF>40$) for As and Cu. For Ni and Cr, they exhibit moderate to significant enrichment. The EF values of Cd are extremely high in the whole of the study area. However, the enrichment factor values of Pb and Zn are moderate to extremely high. Moreover, the distribution of FE in Pb and Zn shows an extreme contamination, mainly in the area surrounding Oued Kasseb and at its downstream due to lead and zinc discharges from the Djebel Hallouf-Sidi Bouaoune mine in Oued Kasseb.

The distribution of EF demonstrates high contamination in the study area, especially around the mine and at the downstream of the mine site. These results are consistent with those obtained by numerous studies conducted at other sites (Mlayah et al., 2009; Boussen et al., 2010). The source of this contamination in the surface sediments of Oued Kasseb catchment originated probably from the alteration and erosion of the mining waste rich in trace metals.

4.4.3 Contamination Factor

The contamination factor (CF) was utilized to indicate the degree of pollution. Its values for the selected

Table 8 Geoaccumulation idex (Igeo), Enrichment facror (EF), and contamination factor (CF) values in surface sediments from Oued Kasseb catchment

	Igeo (As)	Igeo (Cd)	Igeo (Cr)	Igeo (Cu)	Igeo (Ni)	Igeo (Pb)	Igeo (Zn)	EF (As)	EF (Cd)	EF (Cr)	EF (Cu)	EF (Ni)	EF (Pb)	EF (Zn)	CF (As)	CF (Cd)	CF (Cr)	CF (Cu)	CF (Ni)	CF (Pb)	CF (Zn)
S1	2.92	3.42	0.34	-1.53	-0.27	0.48	0.28	42.22	59.61	7.08	1.94	4.64	7.78	6.78	11.33	16,0	1.9	0.52	1.25	2.09	1.82
S2	2.83	3.32	-0.22	-1.31	-0.15	0.29	-0.47	43.12	60.64	5.22	2.44	5.48	7.42	4.37	10.67	15,0	1.29	0.6	1.36	1.84	1.08
S3	3.69	3.22	-0.51	-1.1	-0.32	1.42	0.07	80.2	58.08	4.36	2.9	5,0	16.64	6.53	19.33	14,0	1.05	0.7	1.21	4.01	1.57
S4	5.68	4.06	-0.05	-0.34	0.12	5.93	4.63	234.57	76.49	4.44	3.63	4.99	279.95	113.3	76.67	25,0	1.45	1.19	1.63	91.5	37.03
S5	3.83	4.94	0.16	-1.21	-0.22	3.95	2.69	89.48	192.94	7.03	2.72	5.41	97.16	40.68	21.33	46,0	1.68	0.65	1.29	23.16	9.7
S6	1.83	3.12	0.16	-1.47	0.04	0.58	-0.52	20.15	49.11	6.32	2.04	5.84	8.44	3.96	5.33	13,0	1.67	0.54	1.55	2.24	1.05
S7	4.96	6.24	-0.04	-0.35	-0.22	5.84	4.53	270.33	654.57	8.44	6.81	7.47	497.66	201.17	46.67	113,0	1.46	1.18	1.29	85.91	34.73
S8	4.32	5.3	0.48	-0.56	0.29	4.3	2.92	119.5	235.01	8.35	4.06	7.29	117.39	45.13	30,0	59,0	2.1	1.02	1.83	29.47	11.33
S9	8.76	8.38	0.15	1.35	-0.59	9.87	5.97	6083.74	4679.8	15.62	35.79	9.31	13,158.5	878.01	650,0	500,0	1.67	3.82	1,0	1405.88	93.81
S10	8.43	8.53	0.3	1.45	-0.53	9.32	6.3	4360.47	4665.93	15.49	34.47	8.74	8060.91	994.15	518.67	555,0	1.84	4.1	1.04	958.82	118.25
S11	9.17	8.5	-0.96	1.09	-1.11	9.49	6.34	15,987.06	10,034.95	14.18	59.1	12.82	19,857.22	2242.2	866.67	544,0	0.77	3.2	0.7	1076.47	121.55
S12	6.57	6.01	1.04	-0.7	0.28	6.9	4.32	509.52	346.43	11,0	3.3	6.52	639.56	107.15	142.67	97,0	3.08	0.92	1.83	179.08	30,0
S13	5.52	4.62	-0.02	-1.24	-0.12	5.98	2.29	264.1	142.31	5.67	2.45	5.33	364.98	28.15	68.67	37,0	1.47	0.64	1.39	94.89	7.32
S14	0.83	3.5	0.43	-1.61	0.1	0.69	0.75	10.94	69.76	8.28	2.02	6.61	9.95	10.37	2.67	17,0	2.02	0.49	1.61	2.42	2.53
S15	-2.17	3.22	0.05	-1.54	0.03	-0.22	-0.51	1.08	45.47	5.05	1.68	4.97	4.18	3.42	0.33	14,0	1.55	0.52	1.53	1.29	1.05
S16	-0.1	3.58	0.66	-1.4	0.21	1.56	0.46	4.59	59.07	7.79	1.86	5.68	14.54	6.78	1.4	18,0	2.37	0.57	1.73	4.43	2.07
S17	-2.17	3.5	1.19	-1.43	0.3	-0.05	0.02	1.37	69.76	14.08	2.28	7.57	5.94	6.24	0.33	17,0	3.43	0.56	1.85	1.45	1.52
S18	-2.17	3.32	1.1	-1.63	0.19	0.21	0.32	1.65	74.22	15.9	2.39	8.49	8.59	9.29	0.33	15,0	3.21	0.48	1.72	1.74	1.88
S19	7.5	8.61	-0.98	1.17	-0.22	7.76	6.39	3895.96	8449.24	10.94	48.54	18.5	4678.79	1809.24	270.67	587,0	0.76	3.37	1.29	325.05	125.69
S20	7.46	7.77	0.28	0.07	-0.25	8.48	5.52	1603.63	1991.35	11.08	9.62	7.67	3264.46	418.03	263.33	327,0	1.82	1.58	1.26	536.06	68.65
S21	-0.68	3.5	0.66	-1.68	0.12	0.49	-0.02	3.24	59.05	8.21	1.63	5.66	7.29	5.15	0.93	17,0	2.36	0.47	1.63	2.1	1.48
S22	-2.17	3.5	1.32	-1.09	0.44	0.26	0.42	1.4	71.46	15.72	2.96	8.58	7.57	8.44	0.33	17,0	3.74	0.7	2.04	1.8	2.01
S23	-2.17	2.87	0.71	-1.82	0.32	-0.44	-0.8	1.38	45.43	10.16	1.75	7.74	4.57	3.57	0.33	11,0	2.46	0.42	1.88	1.11	0.86
S24	-2.17	2.74	-0.82	-1.95	-0.59	-1.28	-1.58	1.79	53.67	4.57	2.08	5.34	3.32	2.7	0.33	10,0	0.85	0.39	1,0	0.62	0.5
S25	-1.32	2.74	0.65	-1.39	0.63	1.05	-1.58	3.56	59.38	13.93	3.4	13.75	18.48	2.97	0.6	10,0	2.35	0.57	2.32	3.11	0.5
S26	7.27	8.31	1.17	1.11	0.4	8.2	6.36	1345.93	2774.23	19.7	18.93	11.51	2568.91	716.04	230.93	476,0	3.38	3.25	1.98	440.77	122.86
S27	7.33	7.1	1.05	0.31	0.42	8.19	4.55	1219.96	1038.2	15.68	9.35	10.13	2207.63	177.35	242.07	206,0	3.11	1.86	2.01	438.04	35.19
S28	4.65	5.25	0.72	-1.17	0.15	4.51	4.56	168.79	255.42	11.06	2.99	7.44	153.18	158.62	37.67	57,0	2.47	0.67	1.66	34.18	35.4
S29	3.93	5.3	0.86	-1.02	0.39	2.45	4.75	106.18	274.75	12.69	3.45	9.17	38.3	188.39	22.8	59,0	2.73	0.74	1.97	8.22	40.45
S30	2.3	3.12	0.5	-1.3	0.28	-0.29	-0.2	26.99	47.41	7.73	2.22	6.64	4.46	4.77	7.4	13,0	2.12	0.61	1.82	1.22	1.31
S31	3.5	2.74	0.79	-1.53	0.36	1,0	0.03	70.87	41.85	10.82	2.18	8.06	12.56	6.42	16.93	10,0	2.59	0.52	1.93	3,0	1.53
S32	-0.68	2.74	-0.05	-1.29	-0.32	-1.14	-0.89	4.48	47.98	6.94	2.94	5.78	3.27	3.87	0.93	10,0	1.45	0.61	1.21	0.68	0.81

trace metals (As, Cd, Cr, Cu, Ni, Pb and Zn) are listed in Table 8.

They range from 0.3 to 866.7 for As; from 10 to 587 for Cd; from 0. 8 to 3.7 for Cr; from 0.4 to 4.1 for Cu; from 0.7 to 2.3 for Ni; from 0.6 to 1405.9 for Pb and from 0.5 to 125.7 for Zn. Table 7 also shows that the mean values of the CF in the surface sediments decrease as follows: Pb (180.1) > Cd (122.7) > As (111.5) > Zn (28.6) > Cr (2.1) > Ni (1.6) > Cu (1.2).

Although the CF reflects the individual impact of each heavy metal on the sediments, it is an important tool used to monitor heavy metal pollution (Marove et al., 2022). According to the CF, the surface sediments of Oued Kasseb catchment exhibit different levels of contamination related to the proportions of harmful elements. The results of calculating the contamination factor prove that Ni represents low to moderate contamination in the surface sediments. The CF values show low to considerable contamination by Cr and Cu. For the As, Pb and Zn, while the contamination in the surface sediments of Oued Kasseb catchment varies from low to very high. On the other hand, Cd presents a very high contamination of all samples of Oued Kasseb catchment.

The distribution of CF reveals that the study area is heavily polluted by As, Cd, Pb and Zn, mainly in and around the old mine and the downstream of Oued Kasseb. It can be, therefore, deduced that high contamination by toxic elements deteriorates the river water quality.

4.5 Evaluation of the Ecological Risk

The potential ecological risk indexes (E_r and RI) were calculated to evaluate the contamination levels of each trace element (E_r) and the amount of heavy metals (RI) in the surface sediments of Oued Kasseb catchment. The assessment results are illustrated in Table 9.

The potential ecological risk index (E_r) gave an average value of 4.5, 5.9 and 7.8, indicating a low risk ($E_r < 40$) for Cr, Cu and Ni, respectively. The E_r is from low to considerable for the Zn (Mean: 28.6). However, it varies from low to significantly higher for As, Cd and Pb. On the other hand, the E_r average values of As, Cd and Pb are above 320 ($E_r > 320$), revealing a higher to significantly higher ecological risk in the entire study area for Cd. The E_r values of As and Pb show that highest lever is present, particularly near the old mine and at the downstream of Oued Kasseb.

At Oued Kasseb upstream and Medjerda River, the potential ecological risk index (RI) values range between 315.5 and 30,511.6 with and average of 5741.6. The RI values are between 300 and 600, representing high ecological risk. However, in areas around the old mines, the RI values are above 600, exhibiting significantly higher ecological risks.

In general, the potential ecological risk indexes (E_r and RI) reveal that the highest ecological risk values were recorded in the mine's surroundings and at its downstream areas.

4.6 Human Health Risk Assesment

A Human health risk quotient was used to evaluate how the human health is affected negatively by heavy metal exposure. It allows the quantification and assessment of the cancer-causing and non-cancerous risks through inhalation, ingestion and dermal contact.

The human health risk assessment was carried out to discriminate carcinogenic heavy metals and exposure routes in urban environments (El-Alfy et al., 2021; El-Zeiny & Abd-Hamid, 2022).

4.6.1 Non-Carcinogenic Risk Assessment

The calculated hazar quotient (HQ) values of heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) in Oued Kasseb surface sediments catchment are illustrated in Table 10. The obtained findings reveal that the three metal exposure pathways for both children and adults are reduced in the following order: ingestion > dermal > inhalation. The HQ inhalation and HQ dermal contact values indicate that HQ < 1 for both adults and children for all heavy metals, demonstarating no noncarcinogenic health risk. However, the HQ ingestion showed that HQ of As and Pb is superior to 1 for children and that of Pb exceeds 1 for adults, which constitutes a potential noncarcinogenic health risk.

The results obtained using the hazard index (HI) of heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) in the surface sediments of Oued Kasseb catchment are reported in Table 7. The order of the HI values for heavy metals in Oued Kasseb surface sediments catchment is as follwos: Pb > As > Cr > Cd > Zn > Ni > Cu, both for children and adults. The HI of adults' group reveals an acceptable level of all trace metals (HI < 1), except Pb (HI > 1). However, the hazard

Table 9 Potential ecological risk factor E_r and RI of trace metals in surface sediments from Oued Kasseb catchment

S1				E_r				RI
	As	Cd	Cr	Cu	Ni	Pb	Zn	
	113.33	480	3.80	2.60	6.23	10.44	1.82	618.22
S2	106.67	450	2.58	3.02	6.78	9.18	1.08	579.30
S3	193.33	420	2.10	3.50	6.03	20.06	1.57	646.59
S4	766.67	750	2.90	5.94	8.15	457.50	37.03	2028.19
S5	213.33	1380	3.35	3.24	6.45	115.82	9.70	1731.90
S6	53.33	390	3.35	2.70	7.73	11.18	1.05	469.33
S7	466.67	3390	2.91	5.88	6.45	429.56	34.73	4336.20
S8	300.00	1770	4.19	5.10	9.15	147.35	11.33	2247.13
S9	6500.00	15,000	3.34	19.12	4.98	7029.41	93.81	28,650.65
S10	5186.67	16,650	3.69	20.50	5.20	4794.12	118.25	26,778.42
S11	8666.67	16,320	1.54	16.02	3.48	5382.35	121.55	30,511.60
S12	1426.67	2910	6.16	4.62	9.13	895.38	30.00	5281.96
S13	686.67	1110	2.95	3.18	6.93	474.47	7.32	2291.51
S14	26.67	510	4.03	2.46	8.05	12.12	2.53	565.86
S15	3.33	420	3.11	2.58	7.65	6.44	1.05	444.17
S16	14.00	540	4.75	2.84	8.65	22.15	2.07	594.45
S17	3.33	510	6.86	2.78	9.23	7.24	1.52	540.96
S18	3.33	450	6.43	2.42	8.58	8.68	1.88	481.31
S19	2706.67	17,610	1.52	16.86	6.43	1625.26	125.69	22,092.43
S20	2633.33	9810	3.64	7.90	6.30	2680.29	68.65	15,210.11
S21	9.33	510	4.73	2.34	8.15	10.50	1.48	546.53
S22	3.33	510.00	7.48	3.52	10.20	9.00	2.01	545.54
S23	3.33	330.00	4.92	2.12	9.38	5.53	0.86	356.14
S24	3.33	300.00	1.70	1.94	4.98	3.09	0.50	315.54
S25	6.00	300.00	4.69	2.86	11.58	15.56	0.50	341.19
S26	2309.33	14,280.00	6.76	16.24	9.88	2203.85	122.86	18,948.92
S27	2420.67	6180.00	6.22	9.28	10.05	2190.21	35.19	10,851.62
S28	376.67	1710.00	4.94	3.34	8.30	170.91	35.40	2309.55
S29	228.00	1770.00	5.45	3.70	9.85	41.12	40.45	2098.57
S30	74.00	390.00	4.24	3.04	9.10	6.12	1.31	487.81
S31	169.33	300.00	5.17	2.60	9.63	15.00	1.53	503.26
S32	9.33	300.00	2.89	3.06	6.03	3.41	0.81	325.53

Table 10 Hazard quotient (HQ) and hazard index (HI) values of heavy metals for children and adults

	Children			HI Children	Adults			HI Adults
	HQ ing	HQ inh	HQ derm		HQ ing	HQ inh	HQ derm	
As	7.129	0.000	0.028	7.157	0.764	0.000	0.057	0.821
Cd	0.157	0.000	0.001	0.158	0.017	0.000	0.001	0.018
Cr	0.309	0.001	0.025	0.334	0.033	0.000	0.050	0.084
Cu	0.009	0.000	0.000	0.009	0.001	0.000	0.000	0.001
Ni	0.020	0.000	0.000	0.020	0.002	0.000	0.000	0.002
Pb	11.183	0.000	0.119	11.303	1.198	0.000	0.243	1.442
Zn	0.087	0.000	0.001	0.087	0.009	0.000	0.001	0.011

index of the children's group indicates a potential noncarcinogenic effects risk ($HI > 1$) for As and Pb. In fact, Pb presents a potential non cancerogen risk for both children and adults. The Pb leads to significantly serious health problems, notably encephalopathy, kidney diseases and neuropathy (Caravanos et al., 2006; El-Zeiny & Abd El-Hamid, 2022).

The obtained findings show that the HQ and HI values among children are higher than those of HI among adults, knowing that the larger the HI value is, the higher and the risk. In fact, the population of children is above acceptable levels for health risk assessment. Therefore, we may conclude that, compared to the adults, children are more susceptible to the noncarcinogenic risk caused by the exposure to heavy metal, which may be due to their daily habits and physiological activity (Jiang et al., 2017).

4.6.2 *Cancer Risk Assessment*

In the surface sediments of Oued Kasseb catchment, the results of calculating the cancer risk (CR) index and that of the total cancer risk (TCR) are reported in Fig. 5.

They represent the findings of carcinogenic risk (CR) assessment of ingestion, inhalation and dermal contact for children and adults. According to the provided data, the CR of As, Cr, Ni and Pb ingestion for children is greater than 10^{-4}, indicating that it provides a cancer risk to children living in the region. The CR for of dermal contact is between 10^{-6} and 10^{-4} for As, Cr and Ni, showing an acceptable risk. However, the CR inhalation for children is less than 10^{-6}, revealing that there is no obvious health risk.

The As heavy metal value of CR ingestion presents higher danger ($CR > 10^{-4}$) for adults. In fact, the CR values of Cd, Cr, Ni and Pb vary between 10^{-6} and 10^{-4}, which is an acceptable risk range. As, Cr, Ni and Pb have CR dermal contact values of $10–6 < CR < 10^{-4}$, reflecting a tolerable risk. However, the CR inhalation values for adults are less than 10^{-6}, indicating no risk for human health. Thus, the most important contributors to cancer risk for both adults and children were ingestion, dermal exposure and then inhalation exposure.

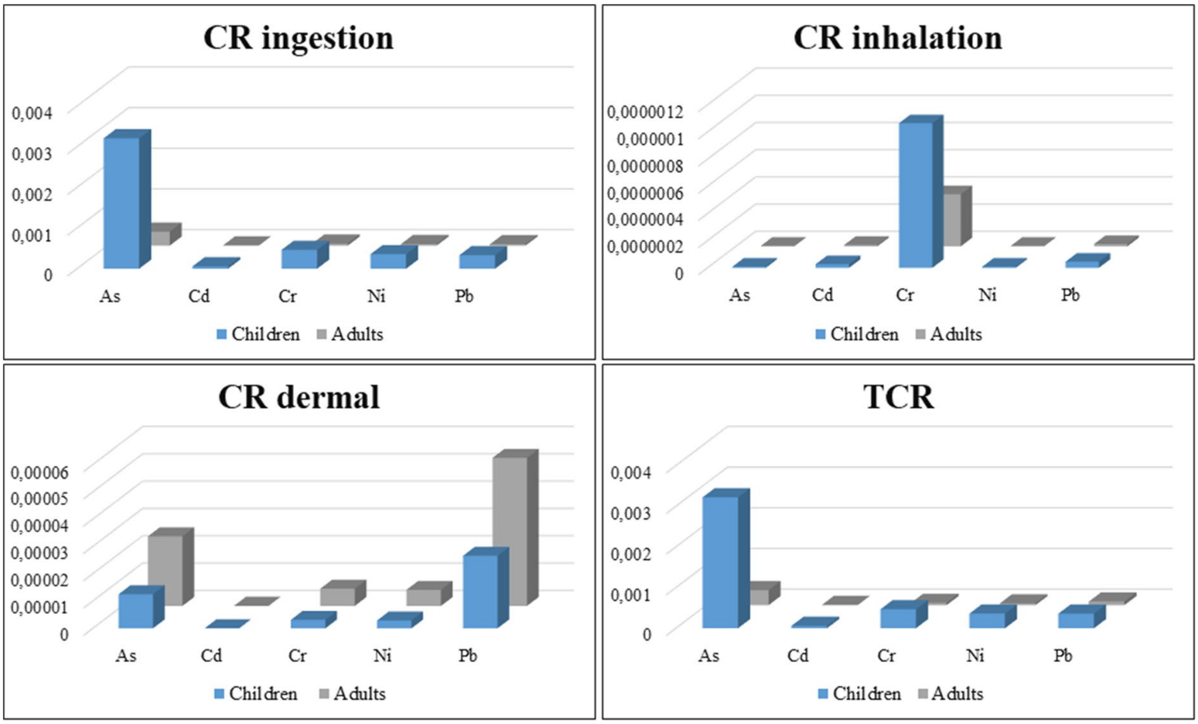


Fig. 5 Cancer risk (CR) and total cancer risk index (TCR) of heavy metals from surface sediments of Oued Kasseb

Based on the total carcinogenic risk (TCR) values of heavy metals in the surface sediments of Oued Kasseb catchment, the average TCR of each element for children is As > Cr > Ni > Pb > Cd and that for adults is As > Pb > Cr > Ni > Cd.

TCR values of Cd for children, ranging between 10^{-6} and 10^{-4}, indicate acceptable levels of Cd. However, those of As, Cr, Ni and Pb are greater than the allowed limit of TCR > 10^{-4}, demonstrating a significant carcinogenic risk resulting from these metal elements in the study area. The TCR > 10^{-6} for the As indicates a high carcinogenic risk in adults, according to the results of the study. Thus, the As is the largest contributor to the overall carcinogenic risk. The arsenic (As) is a global public health threat and a serious contaminant of drinking water (Jiménez-Oyola et al., 2023).

Irrespective of the non-cancer and the cancer risks, it was found that children are more vulnerable to the potential health risk posed by the presence of heavy metals in the surface sediments of the study area (Diami et al., 2016).

Various indices have been used to assess the ecological and human health risks associated with heavy metals (Doležalová Weissmannová et al., 2019; Faiz et al., 2012; Belo et al., 2018 et Diwa et al., 2023). These are currently the most widely used indices in many studies (Diwa et al., 2023). High concentrations of heavy metals in sediments can accumulate and migrate into water. This leads to high toxicity and harmful effects on human health. Therefore, the presence of heavy metals in the sediments of the Oued Kasseb and the Medjerda should be carefully monitored in order not to pose an ecological and health risk to this aquatic ecosystem, intended for irrigation and human consumption.

4.7 Recommandations

The abandonment of Pb–Zn mine of Sidi Alouane in 1986 was a missed opportunity for adequate mine rehabilitation, exposing mining waste to the environment and vice versa (Motswaiso,0.2019). Mostly Cd, As, Pb and Zn, contaminates the sediments of Medjerda River as well as those of its tributary oued Kasseb. So, based on our findings in this study, we recommend:

- To establish national soil and sediments standard and soil and sediments background to assess and monitor the contamination level of heavy metals near abandoned mine sites.
- We suggest a regular monitoring of soil surface, surface water, stream sediment and groundwater quality in order to guarantee that the level of contamination remain lower than the limits

The results of this study can be used by the local government in land use planning and evaluating the future expansion of residential areas/or agriculture in the surrounding area.

5 Conclusion

This investigation of heavy metals was carried out to assess the anthropogenic and industrial consequences and dangers caused by the waste discharges and the mining activities.

Heavy metals in the surface sediments of the Oued Kasseb catchment were evaluated based on the distribution of some trace metals such as As, Cd, Cr, Cu, Ni, Pb, Zn, and Pb. The obtained results indicated that the mean concentrations of heavy metals in the surface sediments were approximately equal to 167.3, 12.3, 72.4, 29.3, 31.1, 3061, 4, and 2031.3 mg/kg, respectively. The performed analysis showed high values of metals concentrations in the surface sediments than the UCC for the majority of heavy metals, except in some stations near Medjerda River. The sediment pollution assessments, relying on Igeo, EF and CF indices, revealed high levels of contamination, mainly in and around the old mine and at the downstream of Oued Kasseb. The spatial distribution of heavy metal concentrations and pollution indices in the surface sediment samples showed that the highest values of heavy metals in the surface sediments were registred around the old mining area. These values decreased near Mejerda River. It was also obvious that the sediment quality degradated as a result of the pollution caused by heavy metal, making it difficult to manage the pollution/contamination area. In fact, heavy metal contaminations resulted from the anthropogenic sources such as wastewater irrigation, industrial pollutants and chemical manufacturing. The statistical analysis confirms the results obtained by showing a significant correlation between metals (As, Cd, Cr, Cu, Pb, Zn and Pb). The metals with high correlation coefficients exhibited comparable behaviour under similar environmental conditions due to the abandoned mine, the inputs from the urban areas and the pesticide use in farming. Positive contributions from Cr and Ni suggest that the above-mentioned metals may be of natural origin and can be influenced by erosion, water runoff and other factors such as the adjacent land alteration. The health risk assesment indices reveled a noncancerogen risk and high risk of arsenic for children. However, the obtained total cancerogenic risk value of As is unacceptable for adults and children. The high levels of As have both natural and anthropogenic origins. Based on the spatial distribution of the heavy metals, it was obvious that the abandoned Pb–Zn mine is the main source of the heavy metals in the surface sediments of Oued Kasseb catchment. However, it was proven that the anthropogenic activities, the discharges from the Bousalem city, the use of pesticides in the adjacent farmland as well as the erosion and the run-off do not significantly affect the surface sediments by the heavy metals. Finally, we may conclude that the large amounts of heavy metals pose high risks to the public health and the environment. In general, the wastes released from the abandoned Pb–Zn mine in Jebel Hallouf-Boulaouane are subject to erosion, endanger the quality of the soil and sediments, degrade water quality in the area's aquatic environments and, thereby, represent a serious threat to the human health. Indeed, the mining waste has great potential to damage the aquatic ecosystems and, in turn, the human health as well as the whole environment.

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Declarations

Ethics approval and consent to participate Not applicable.

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