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Assessment of potentially trace metals contamination in watersheds of the eastern Mitidja plain, Algeria

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Abstract

Water pollution is a global issue that threatens water security, affecting not only human health but also the environment and biodiversity. The work was conducted to assess the degree and sources of potentially trace metals (PTMs) contamination from the main river tributaries of the eastern Mitidja plain. Seventeen sites were selected for water sampling. The mean concentrations of PTMs in water over all the sampling sites were Cd 15.3, Cr 122, Cu 37.7, Fe 708, Ni 30.2, Pb 69.9 and Zn 133 µg/l. The overall mean concentration of PTMs in surface water showed the following order Fe > Zn > Cr > Pb > Cu > Ni > Cd. Based on the metal index, the results indicate that water quality is unsuitable for drinking purposes. For irrigation use, MI values indicate spatial variability in contamination levels, with conditions varying from slight to strong impact across sampling sites. Principal Component Analysis identified three main factors or sources that determine the relative abundance of trace metals. Excluding atmospheric deposition and runoff from agricultural areas, industrial and urban wastewater discharge and discharge from uncontrolled, solid-waste landfills are probably the main sources of water contamination. The findings of this study highlight the need to adopt environmental measures to reduce and control TM concentrations in the river water of the area. This includes implementing strict policies to manage industrial and urban waste, as well as promoting sustainable agricultural practices to minimize polluting runoff.

Keywords: contamination; metal index; multivariate statistics; Mitidja plain; potentially trace metals; water quality.

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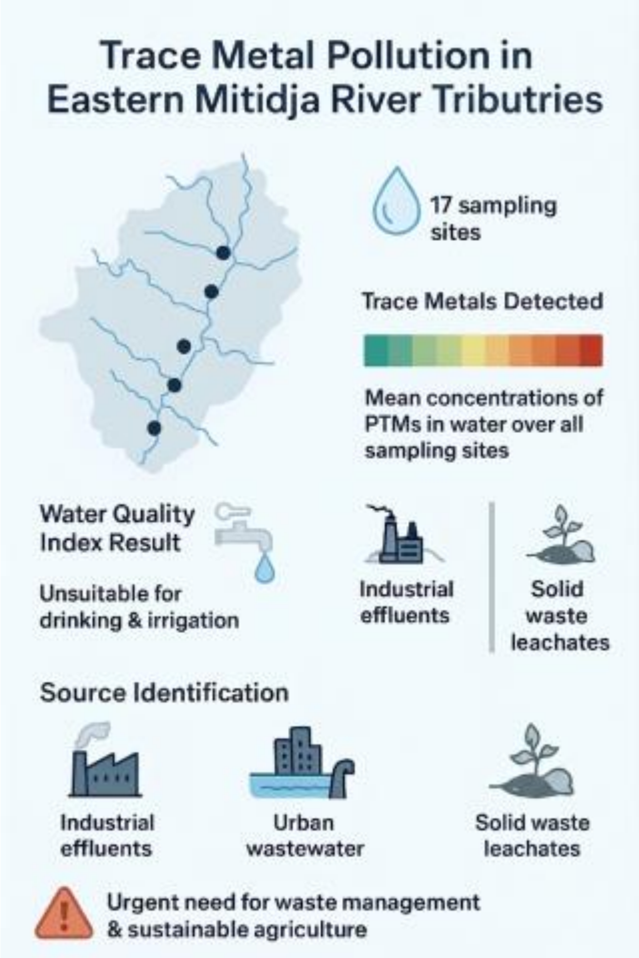
Graphical abstract



1. Introduction

The trace metals (TMs) in the surface waters system come from geochemical weathering and anthropogenic activities such as mining, agriculture and industry (Greenfield *et al.* 2012). In the last three decades Algeria has undergone urban and industrial growth, which may have altered the chemical quality of surface waters (Kerboub and Fehdi 2014) including the Mitidja plain, an important agricultural production area. Numerous industrial units have been established along the main rivers, namely El Harrach, El Hamiz and the Reghaia rivers. The main anthropogenic sources observed in the study area were associated with metallurgical activities, building materials, petrochemicals, pharmaceuticals, electrical and electronic industries, and food industry and paper (Laribi and Saidani 2016; Laribi *et al.* 2019). However, these activities generate wastewater containing PTMs, pesticides, hydrocarbons etc. that receives little or no treatment before discharge leading to degradation of the quality of the aquatic environment. Indeed, the PAC report (2005) revealed that only 8% of wastewater (225-million m^3 yr^{-1}) discharged in the Bay of Algiers is treated. In 2017, only 51 industrial units out of 156 operating in the Wilaya of Algiers have sewage treatment plants (AE 2017).

To regulate the use of water and protect the natural environment, Algeria has several regulations including Law No. 05-12 (2005) on water and the Executive Decree No. 11-219 (2011) on the quality of surface water intended for drinking water supply. Studies reported Trace metals contamination of El Harrach river and the sediments of the Algiers Bay have been reported (Benamar *et al.* 1999) and mainly related to uncontrolled discharges of industrial and domestic effluents (Yoshida *et al.* 2005). In developing countries, mining activities and the release of insufficiently treated industrial wastewater are among the main sources of metal contamination in freshwater systems (Dutta *et al.* 2021). The presence of PTMs at concentrations above the maximum allowable concentration may cause toxicity to aquatic fauna and flora and pose a significant risk to public health through the food chain (Samai *et al.* 2023). Therefore, an assessment of the potential sources and concentrations of PTMs in surface waters is required to aid future control and manage the contaminated sites.

Two complementary approaches, qualitative and quantitative, have been proposed to assess the PTMs contamination of waters (Huang *et al.* 2016; Ogunkunle *et al.* 2016). The qualitative approach is based on the application of multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis (CA) to interpret the environmental data and provide some insights into controls on water quality (Bilgin and Konanç 2016; Custodio *et al.* 2020). The quantitative approach concerns the application of environmental quality indicators such as the pollution indices. For example, Goher *et al.* (2014) evaluated the water quality of the Ismalia Canal in the Nile River based on the metal index (MI). The principle of this approach is based on the comparison of measured concentrations of PTMs in water with their regulatory limit values in irrigation water (USEPA 2012) and drinking water (WHO 2011). Similarly, the study conducted by Ogunkunle *et al.* (2016) using MI, revealed that the surface water of the four earthen dams in llorin, north central Nigeria, were seriously affected by Pb and Cd (> 6.0 for both metals). Other authors have suggested the use of both approaches to assess water contamination (Boateng *et al.* 2015; Kumar *et al.* 2018).

The objective of our work was to assess the level of water contamination and to identify the sources of trace metals using multivariate statistics and MI. To our knowledge, this is a first work in the Mitidja plain that uses both approaches and addresses the problem of water contamination by TMs at the regional level.

2. Materials and Methods

2.1. *Study Area*

The Mitidja plain is located close to the city of Algiers. It is limited to the south by the foothills of the Atlas and to the north by the ride of the Sahel and the Mediterranean Sea. It covers an area of 1400 km^2 and its length is about 100 km with a width that varies from 5 to 20 km. Our study concerned the eastern part of the Mitidja plain, with a total area of 665 km^2. The study area is centred on 3° 10' 25.58'' E and 36° 39' 47.73'' N. The watershed of the eastern Mitidja plain is divided into three sub-catchments, namely Reghaia, Hamiz, and El Harrach. The hydrographic network is dense, characterized by the following main tributaries: El Harrach river, El Hamiz river and Réghaia river. All of these tributaries originate in the Atlas Mountains with a South-North flow direction. The climate of the region is subhumid Mediterranean type with two seasons: a wet and cold season (September to May) and a hot and dry season (June to August), and the mean annual rainfall is 600 mm. The mean temperature is 18.1^{0}C. From a geological point of view, the Mitidja is a subsidence zone filled with plio-quaternary deposits.

2.2. *Location of sampling sites and water analysis*

To evaluate the effect of human influence on TM concentrations in surface waters, seventeen sampling sites were selected for water samples during the winter season. The position of each sampling point was recorded using a portable global positioning system (model Garmin ester 10, Europe Ltd, Southampton, UK).

The distribution of sampling points is shown in the **Figure 1**. The choice of sampling sites was based on the nature of the water, accessibility, and their location in relation to anthropogenic activities. Water samples were collected during the winter season from 5 to 7 January 2015, in a single sampling campaign. This study is limited to a single winter sampling campaign. Therefore, seasonal variability in TM concentrations was not evaluated.

At each site, a water sample was collected at a depth of 10 cm using 1.5 L a polyethylene bottle, placed in a cooler at 0-4^{0}C and transported to the laboratory immediately for chemical analysis. Prior to water sampling, the bottles were rinsed first with distilled water and then with water from the site. Physico-chemical parameters such as pH and electrical conductivity (EC) were performed in laboratory within 24 hours after collecting the sample using HANNA instruments. For TE analysis the water samples were filtered through a 0.45 µm Whatman membrane filters meaning that the reported concentrations correspond to the dissolved fraction of trace metals. After filtration, samples were acidified with analytical grade nitric acid to pH = 2 and stored in a refrigerator (0-4°C.) as suggested by the standard methods. The concentrations of Cd, Cr, Cu, Fe, Ni, Pb and Zn were determined using Perkin Elmer AAnalyst 800 graphite furnace atomic absorption spectrometry.

Quality assurance/quality control procedures were implemented throughout sampling and analysis. Field and reagent blanks were included in each analytical batch to monitor potential contamination. Sample analyses were performed in duplicate to ensure analytical precision. Limits of detection (LOD) and quantification (LOQ) were determined based on replicate measurements of procedural blanks, defined as three and ten times the standard deviation of blank signals, respectively. The LOQs for the different trace metals were (µg/l): 0.07, 0.19, 0.75, 0.15, 0.22, 0.15 and 0.18 for Cd, Cr, Cu, Fe, Ni, Pb and Zn, respectively.

2.3. *Water contamination assessment*

The chemical quality of the water was assessed using the single factor (I) and the metal index (MI)

$$I = \frac{C_i}{S_i} \quad (1)$$

where I is the over-limit ratio of the PTMs in river tributaries of the eastern Mitidja plain, Ci is the tested single PTMs concentration, and Si is the evaluation standard of the TM in the surface water (Zhaoyong *et al.* 2015; Boateng *et al.* 2019).

Metal Index (MI)

Water contamination by trace metals is associated with a cocktail of elements rather than a single metal. The metal index is calculated by the following equation (Goher *et al.* 2014):

$$MI = \sum_{i=1}^{n} \frac{C_i}{(MAC)_i} \quad (2)$$

Where Ci is the concentration of each metal in water (µg/l), MACI is the maximum admissible concentration of each metal in water (µg/l), and I represents the MAC of each metal. As the concentration of TM exceeds the MAC, the quality of water is deteriorated. MI greater than 1 represent a threshold warning (Boateng *et al.* 2019). Six classes have been suggested to assess the suitability of the water quality for drinking and irrigation purpose (Ogunkunle *et al.* 2016):

Class I	Very pure	< 0.3
Class II	Pure	0.3-1
Class III	Slightly affected	1-2
Class IV	Moderately affected	2-4
Classe V	Strongly affected	4-6
Class VI	Seriously affected	> 6.

2.4. *Statistical analysis*

The statistical analysis included descriptive statistics (mean, range, and coefficient of variation), and multivariate statistics such as PCA. The Ryan-Joiner test (R-J) was used to check the normality of all variables. All statistical treatments were performed using Minitab17 and Past3. Prior to the application of multivariate statistics, the datasets were standardized by log-transformation to reduce the influence of anomalously high concentrations and to approximate a normal distribution.

PCA identifies the factors that have contributed most to the construction of the major components. It was performed based on the correlation matrix of chemical parameters. The Kaiser criterion was used to define the number of factors, corresponding to the eigenvalues greater than one after a varimax orthogonal rotation. This type of analysis most often allows the grouping of data with similar characteristics, thus giving clues to the process of water contamination or the origin of trace metals. The interpretation of the PCA results was made based on possible sources of TM (lithogenic, anthropogenic or mixed). The correlation between measured chemical parameters was investigated using the Pearson correlation coefficient. To test the significance of the correlation between TM, the P-Values were compared to significance levels (5% and 1%).

3. Results and Discussion

3.1. *Physico-chemical parameters and concentrations of trace metals in waters*

The results show the electrical conductivity of the water samples ranged from 640 µS/cm (S2, El Hamiz dam) to 1610 µS/cm (S1 El Hamiz River,) with a mean value of 1335 µS/cm indicative of a slight to moderate risk of salinity in the case where these higher conductivity waters are used for agricultural purposes (USEPA 2012).

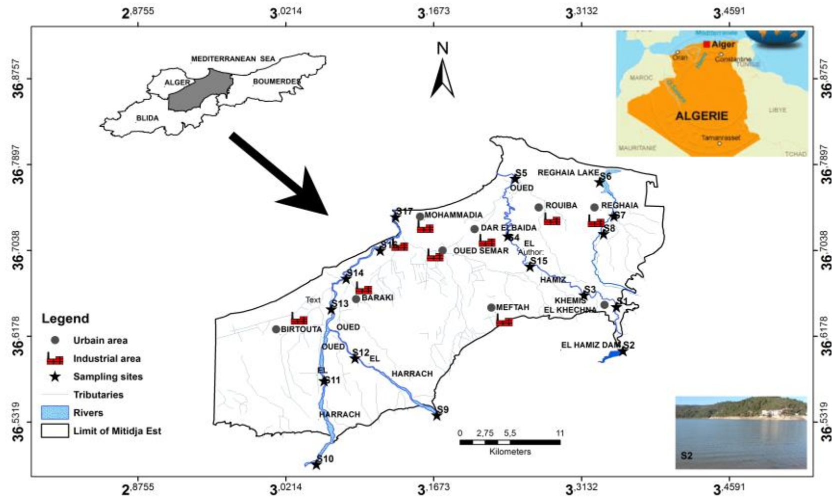


Figure 1. Distribution of water sampling points in the eastern Mitidja plain.

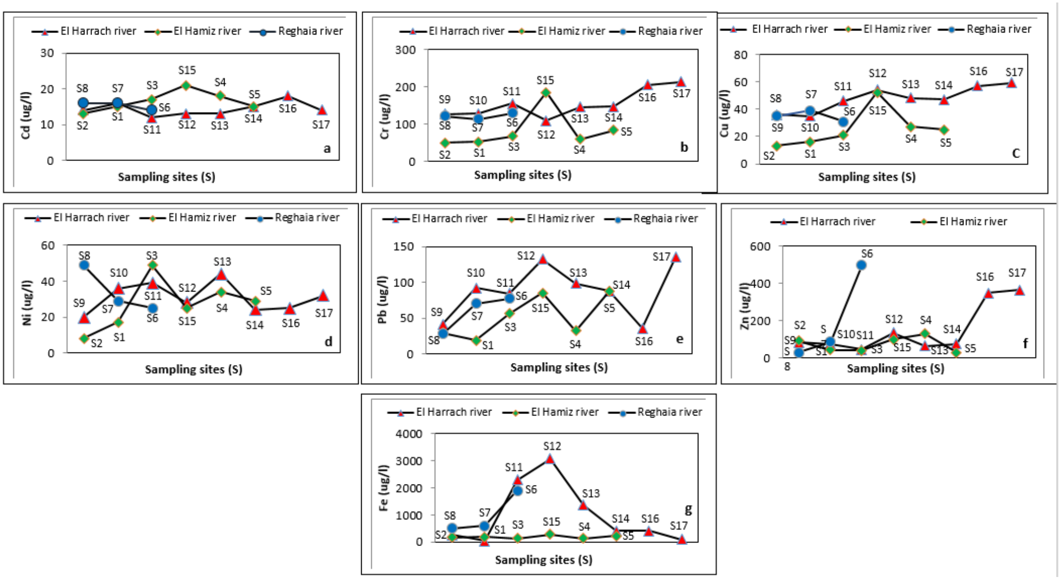


Figure 2. Spatial variation of trace metals in the different streams of the eastern Mitidja plain.

The pH values in the different sites ranged from 7.40 to 7.69 with a mean of 7.56. This alkaline nature of the water is probably related to the presence of carbonates that act as buffers. These pH values are within the recommended range (6.5-8.4) for irrigation water (USEPA 2012).

The TMs analysis results showed a low variability for the concentrations of Cd (CV =15%) indicative of homogeneous distribution of this metal in the corresponding sampling sites and may reflect increased influence of diffuse inputs resulting from atmospheric deposition such as vehicle exhausts, emission from domestic and industrial incineration, and runoff from land area. In contrast the high variability for the concentrations of Cr, Cu, Fe, Ni, Pb and Zn (36% <CV> 127%) suggests a more heterogeneous distribution of these metals over the sampling sites (Boateng *et al.* 2015). The mean concentrations observed for the different elements allowed the following rank: Fe >> Zn > Cr > Pb > Cu > Ni > Cd. Iron and Cd are the most and least abundant elements of the fluvial system. The same trend of element concentrations has been obtained for the sediment of the main tributaries of the eastern Mitidja plain (Laribi *et al.* 2017). The mean concentrations of TMs in the waters exceeds the world mean values in the natural rivers (Gaillardet *et al.* 2003).

Cadmium concentrations ranged from 12 to 21 µg/l with a mean value of 15.3 µg/l. The mean Cd concentration in the study area was greater than the limit values for irrigation water (USEPA 2012) and for drinking water (Executive Decree No. 11-219 2011). These results reflect the evidence of water contamination by Cd, which is in agreement with the results of Cd in sediments (Laribi *et al.* 2017). The highest concentration were observed at S15 (El Hamiz river) and the lowest concentration at S11 (El Harrach river) (**Figure 2a**). Cadmium concentration**s** in the various wastewater discharges from Oran and Mostaganem cities in Algeria have also revealed this element to be above the normative limit of 0.20 mg/l (Remili and Kerfouf 2013). Keria *et al.* (2024) reported that Cd emerged as the primary metals posing the greatest risk to water quality in wetland environments in Algeria. However, concentrations of Cd in the current study (15.3 µg/l) were higher than the concentration values for Europe (5.69 µg/l) and North America (1.12 µg/l), and lower than in Africa (45.05 µg/l), Asia (17.75 µg/l) and South of America (63.54 µg/l) (Zhou *et al.* 2020). Anthropogenic sources of Cd in the environment can be derived from atmospheric deposition, urban and industrial discharges, waste incineration, metallurgical industries, combustion of petroleum products and use of pesticide and fertilizers in agriculture (Forstner and Wittmann 1983; Remili and Kerfouf 2013).

Chromium concentration**s** ranged from 49 to 212 µg/l with a mean value of 122 µg/l. The highest concentration was recorded at the mouth of El Harrach river (S17) (**Figure 2b**). The mean value of Cr in this study was 1.2 times higher than the regulatory values for irrigation water (USEPA 2012) and drinking water supply (Executive Decree No. 11-219, 2011). The disposal of uncontrolled industrial and urban effluents into the River could be the main source of this pollution (Yoshida *et al.* 2005; Kerboub and Fehdi 2014). The presence of Cr in water samples is generally associated with metal industries, chemical industries, galvanic activities and surface treatment activities and tanneries (Forstner and Wittmann 1983). All of these activities have been observed in the study area.

Copper concentrations ranged from 13 to 59 µg/l, with a mean value of 37.7 µg/l 5 (**Figure 2c**). These values remained below the standards set for irrigation water and drinking water supply (Executive Decree No. 11-219, 2011; USEPA 2012). These results are consistent with those of Messaoud Nacer (1987) for Mazafran watershed, who reported Cu concentrations below the World health Organization standard (WHO, 2011).

The results of **Table 1** and **Figure 3d** also showed that the minimum concentration of Ni (8 µg/l) occurred in the waters of El Hamiz river (S2). The maximum concentration (49 µg/l) was observed in both the El Hamiz River (S3) and the Reghaia river (S8). Ni concentrations in water were below the standards for irrigation water (200 µg/l, USEPA 2012) and drinking water (70 µg/l, WHO 2011).

Table 1. Concentration of trace metals (µg/l) in the watershed of the main tributaries of the eastern Mitidja plain

Trace metals	El Harrach river		Reghaia river		El Hamiz river		This study	WMCNW[a]	MCWI[b]	SW[c]	WHO[d]
(µg/l)	Mean	Range	Mean	Range	Mean	Range	Mean				
Cd	14.38	12-18	15.33	14-16	16.5	13-21	15.3	0.08	10	5	3
Cr	153	109-212	121	113-129	82.33	49-184	122	0.7	100	100	50
Cu	47.75	35-59	35	31-39	25.67	13-52	37.7	1.48	200	200	2000
Fe	992.13	43-3078	994.33	493-1900	185	124-283	708	66	5000	ND	2000
Ni	31	20-44	34.33	25-49	27	8-49	30.2	0.8	200	ND	70
Pb	88.25	36-135	58.33	28-77	51.33	19-87	69.9	0.08	5000	50	10
Zn	150	47-365	205.67	32-497	73.83	32-131	133	0.6	2000	5000	3000

[a]*World mean concentration in the natural waters of rivers (Gaillardet et al. 2003).*

[b]*Maximum concentration in water irrigation (USEPA 2012).*

[c]*Quality of surface water intended for drinking water supply (Executive Decree n° 11-219 2011).*

[d]*Threshold values for drinking water according to the World Health Organization (WHO 2011).*

Lead concentrations ranged between 19 and 135 µg/l, with a mean value of 69.9 µg/l. The minimum concentrations of Pb were recorded at S1 (El Hamiz river) and the maximum at S17 (El Harrach river) (**Figure 3e**). The mean Pb concentration of the studied waters exceeded the threshold values for drinking water set by the World Health Organization (WHO 2011) and the current legislation in Algeria (Executive Decree No. 11-219 2011). However, Pb concentrations remained below the maximum allowable concentrations for irrigation water (5000 µg/l, USEPA 2012). Lead concentrations between 2 and 175 µg/l have been reported in the waters of the Nyl River in South Africa (Greenfield et al. 2012) and between 110 to 340 µg/l in the waters of the Ntem watershed in Yaoundé, Cameroon (Defo *et al.* 2016).

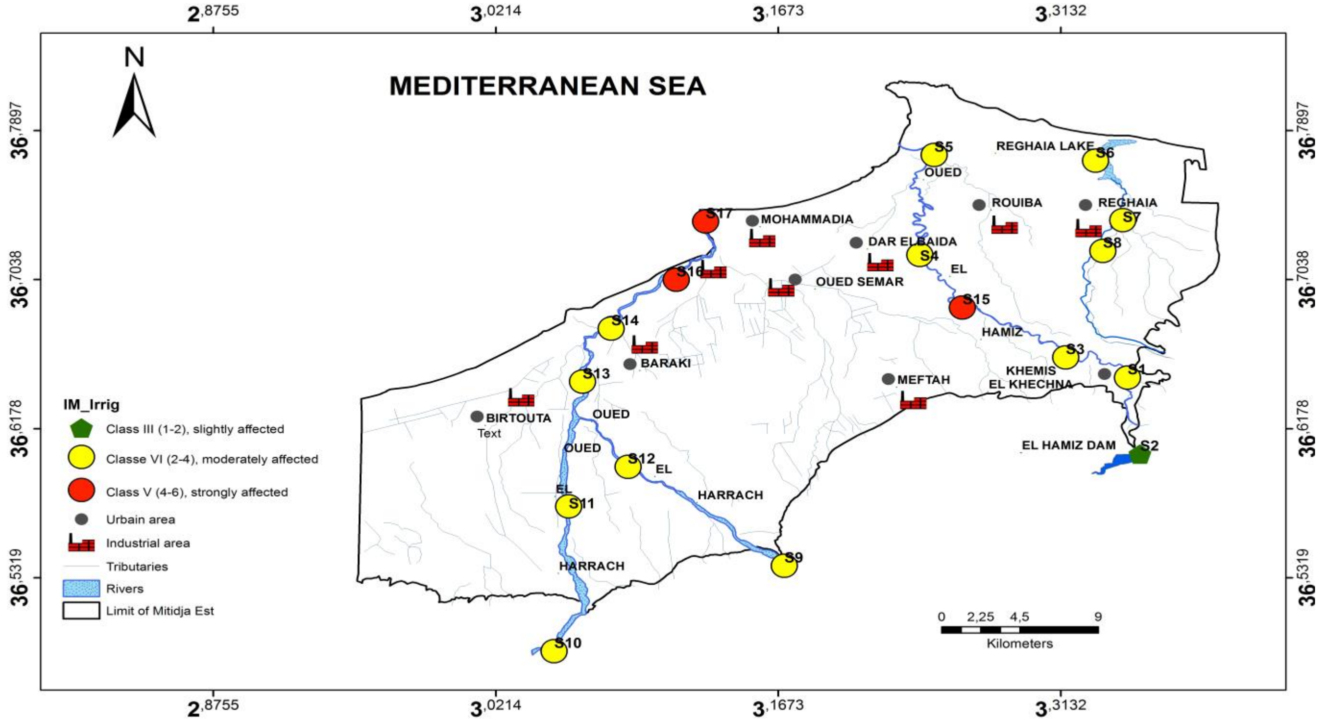


Figure 3. Spatial distribution of the metal index for irrigation water at the different sampling points of the eastern Mitidja plain.

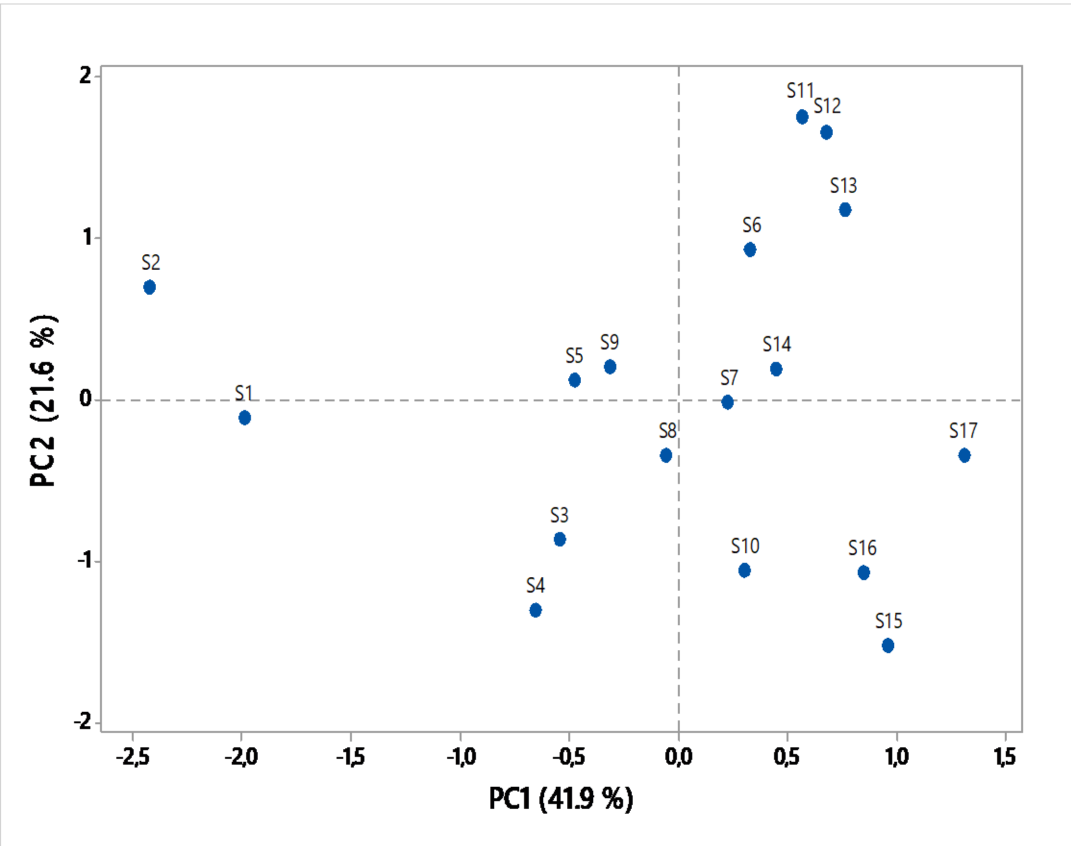


Figure 4. The scores plot (PC1 and PC2) for the water samples.

Zinc concentrations were lower than the recommended standards for drinking water of 3000 µg/l (WHO 2011) and 5000 µg/l (Executive Decree No. 11-219 2011). Similar to Pb concentration values, Zn concentrations remained below the recommended limits for irrigation water (2000 µg/l, USEPA 2012). The maximum concentration of 497 µg/l was found at sample site S6 (Lake of Reghaia) (**Figure 3f**). The minimum concentration (32 µg/l) was measured at both sample site S5 and S8 (El Hamiz River and Reghaia river). Concentrations similar in range (between 0 and 800 µg/l) to this study were reported in the waters of the Mazafran watershed, Mitidja (Messaoud, 1987).

Iron concentrations ranged widely from 43 to 3078 µg/l with a mean value of 708 µg/l (**Figure 3g**). The mean Fe concentration was below the suggested limit values for drinking water supply and irrigation water. Iron is generally more abundant in the aquatic environment than other metals, due in part to its high abundance in the earth's crust (McLennan, 2001). The Fe levels in the waters observed in this study are within the range (200-8000 ug/l) reported for the waters of the Mazafran watershed, Mitidja (Messaoud, 1987).

The overall mean concentration of PTMs in surface water showed the following order Fe > Zn > Cr > Pb > Cu > Ni > Cd. Iron was the element that showed the highest concentrations while Cd recorded the lowest concentrations in the watershed. Similar results are reported for the sediments of the main river of the Mitidja plain (Laribi *et al.* 2017).

3.2. *Single factor (I) and Metal index (MI) in watersheds*

The results showed that the single factor index (I) values for irrigation water were below <1 for Cu, Fe, Ni, and Pb, with the exception of Cd and Cr. A similar trend was observed for drinking water, except that Pb exhibited levels of contamination. The MI values for drinking water ranged from 8.30 to 23.1, with a mean value of 15.4. The highest value of the MI was registered at the sample site S17 of El Harrach river. According to the threshold values set by WHO (2011), these results suggested that all water sampling sites are seriously affected by TM (MI > 6), which make the water unfit for human consumption. In comparison with other studies, the mean value of MI obtained for this study was lower than reported (MI: 47.5-83.0) for the various water dams in the northern central part of Nigeria (Ogunkunle *et al.* 2016).

Regarding irrigation water, the values of the MI ranged from 1.98 to 4.51, with a mean value of 3.31. The highest value of MI was observed at the sample site S16 of El Harrach river (**Figure 3**). The lowest value of MI was obtained at the sample site S2 of El Hamiz Dam.

The results showed that 6% of the sites are slightly affected (class III, 1-2), 76% are moderately affected (class VI, 2-4) and 18% are strongly affected (class V, 4-6) (**Figure 3**). Based on the mean value of MI (3.31), the study area was classified as moderately affected by PTMs. Using the heavy metal evaluation index (HEI), it was observed that 60% of the samples showed elevated pollution levels by trace metals across 16 basins in Algeria (Keria *et al.* 2024). Uncontrolled discharges of industrial and domestic effluents along the banks of the various rivers add significantly to the contamination (Yoshida *et al.* 2005), from atmospheric deposition, leaching and runoff from agricultural areas. Krika and Krika (2017) found that agricultural activities and discharges of domestic wastewater are considered the main sources of waters contamination of the Nile River in the northeast of Algeria.

3.3. *Correlation matrix between trace metals in waters*

Statistical correlations between metals concentrations provide a perspective on TM sources and pathways. A linear correlation coefficient r > 0.7 indicates a strong correlation, while r between 0.5 and 0.7 shows a moderate correlation (Boenteg *et al.* 2015). There are significant statistical correlations between the following pairs of metal concentrations: Cd/Fe ($r = -0.524$; $p < 0.05$), Cr/Cu ($r = 0.898$; $p < 0.01$), Cr/Pb ($r = 0.49$; $p < 0.05$), Cr/Zn ($r = 0.477$; $p \le 0.05$) and Cu/Pb ($r = 0.633$; $p < 0.01$).

Strong correlations between TM concentrations in the water reflect similar release levels from similar sources, and/or identical geochemical behaviour during their transport in the river system. The strong and moderate correlation found between the elements were in agreement with those obtained for sediment by Laribi *et al.* (2017). Lack of statistically significant correlation suggested either different sources of pollution or different geochemical properties (Bilgrin and Konanç 2016). González-Díaz *et al.* (2025) reported that studying the correlations between TM is relevant for understanding common sources of contamination and for highlighting the interactions among these pollutants in the environment, as well as their potential effects on health and ecosystems.

The negative correlation between Fe and Cd concentrations likely reflects contrasting geochemical behaviors in riverine environments, where Cd is immobilized via adsorption and co-precipitation with Fe oxyhydroxides under near-neutral to slightly alkaline conditions. (Martinez and McBride 1998).

3.4. *Assessment of trace metal sources*

The PCA results (**Table 2**) show the first three components explained 81% of the total variance of the data and play a significant role in explaining the TM distribution and contamination source within the study area. From the principal component scores plot it can be shown that the sampling sites in the right quadrants of the scores plot contained higher concentrations of TMs than those at the left quadrant (**Figure 4**). Only loading coefficients (eigenvectors) ≥ 0.5 (**Table 2**) were considered to define the variables that show a correlation with the component (Moore *et al.* 2011).

The first rotated component (PC1) explains 41.9% of the total variance and characterize samples based on Cu, Cr, Pb, and Ni concentrations and can be defined as a mixed source of both natural and anthropogenic origin. The relative contribution of these sources varied among the three sub-catchments. In particular, the El Harrach River showed the highest mean concentrations of Cu, Cr, and Pb, with Cr concentrations generally increasing towards the downstream reaches, where industrial and urban activities are concentrated. Cadmium, Fe and Zn have lower loading factors in the first component suggesting their independency within this group and other impacts. The main sources of Cr emission in the environment are the chemical industry (chrome plating, leather tanning, and pigments) and the metallurgical industry. Tanneries, for example, can generate effluents containing several mg/l of Cr (Forstner and Wittmann 1983). These findings are in accordance with those found by Yoshida *et al.* (2005) who reported Cr contamination for El Harrach river and Oued Semar river. The source of Cr can be attributed to urban and industrial solid waste disposed along the banks and the discharge of uncontrolled industrial and urban effluents (Yoshida *et al.* 2005; Kerboub and Fehdi 2014). As observed for the concentration of Cr, the concentrations of Pb exceeded the threshold values for drinking water and could be attributed to the discharge of industrial effluents and public sewage in the aquatic environment (Boateng *et al.* 2015). Although the concentrations of Cu and Ni remained below the standards for drinking water (WHO 2011) and irrigation water (USEPA 2012) the association of these elements with Cr and Pb indicated that anthropogenic activities contribute to the accumulation of Cu and Ni in the river water of study area.

Table 2. Total variance explained and component matrixes for studied trace metals.

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
Total variance explained									
1	3.012	43.0	43.0	3.012	43.0	43.0	2.935	41.9	41.9
2	1.441	20.6	63.6	1.441	20.6	63.6	1.509	21.6	63.5
3	1.213	17.3	81.0	1.213	17.3	**81.0**	1.222	17.5	**81.0**
4	0.615	8.8	89.9						
5	0.360	5.1	94.9						
6	0.293	4.2	99.1						
7	0.063	0.9	100						

Element	Component matrix			Rotated component matrix		
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3
Cd	-0.092	-0.912	-0.059	0.107	-0.912	0.035
Cu	0.948	-0.155	-0.027	0.957	0.049	-0.068
Ni	0.507	-0.315	0.703	0.590	-0.123	0.698
Pb	0.781	0.124	0.104	0.739	0.298	0.045
Zn	0.432	-0.062	-0.821	0.404	-0.057	-0.836
Cr	0.904	-0.183	-0.132	0.916	0.000	-0.168
Fe	0.484	0.658	0.115	0.333	0.755	0.021

*Extraction method: Principal Component Analysis: Rotation method: Varimax***.**

The second rotated component (PC2) explained 21.6% of the remaining variance (after PC1) and was positively correlated with Fe (0.755) and negatively correlated with Cd (-0.912). The factors for these metals move in the opposite directions, suggesting either different sources or the co-precipitation of Cd with Fe oxides. Given the near-neutral to slightly alkaline pH conditions of the water (7.40–7.69, mean 7.56), Fe is likely to form oxyhydroxides, which enhance the adsorption and possible co-precipitation of Cd. This mechanism may reduce the dissolved Cd fraction as Fe concentrations increase, explaining the observed inverse Fe–Cd relationship.

Cd concentrations in the water were above the threshold values, suggesting a strong influence of anthropogenic sources, although geochemical inputs cannot be excluded. The occurrence of this element at elevated concentrations in the aquatic environment seems to be associated with atmospheric deposition, emission from urban and industrial incineration and agricultural origin (Forstner and Wittmann 1983; Remili and Kerfouf 2013).

The mean concentration of Fe in water was below the recommended threshold values for irrigation water and drinking water. Iron is ubiquitous in soil and therefore the sources of Fe may be attributed to natural lithological sources. In addition, the Fe concentrations did not reveal a significant statistical correlation with the other elements, except for Cd where an inverse relationship was found suggesting a different lithogenic origin for these elements in the water.

The third rotated component (PC3) showed positive loading on Ni (0.698) and negative loading on Zn (-0.836) and explained 17.5% of the remaining variance. These two elements were within the range of normal values established by WHO (2011) and USEPA (2012). In the present study, PC3 may reflect a lithogenic component controlled in part by sedimentary parent materials such as calcareous rock.

The industries that bring TM into river water are tannery, paints, paper, metallurgical activities, building materials, petrochemicals, pharmaceuticals, electrical and electronic industries, and food industry (Forstner and Wittmann 1983), and are located in the central part of El Harrach river. In these sites, high concentrations of Fe were observed.

4. Conclusion

The degree of contamination and potential sources of TEs from the main tributaries of the eastern Mitidja plain were assessed using the MI and multivariate statistical techniques. The trace metals showed a general order of abundance as follows: Fe >> Zn > Cr > Pb > Cu > Ni > Cd. The mean concentrations of Cd and Cr were found at concentrations above the threshold values for drinking water and irrigation water. Cadmium contamination appears to be widespread and affects all sites. Chromium concentrations in water generally increase from upstream to downstream to reach maximum levels at the mouth of El Harrach river. The mean concentration of Pb exceeded the standard limit for drinking water but remained below the limit value for irrigation water. Uncontrolled industrial and urban discharges are, in part, the source of this water contamination. Based on the MI results, the studied waters are classified as unsuitable for drinking purposes, while for irrigation they show a spatially variable degree of impact, ranging from slightly to strongly affected depending on the site. The PCA performed on the concentrations of the seven metals, indicated both lithogenic and anthropogenic activity sources that control the concentrations of TMs in the study area. The first component represented by Cr, Cu, Ni, Pb explained 41.9% of the varaiance, a second component represented by Cd and Fe explained 21.6% variance and a third component formed by Ni and Zn concentrations explained 17.5% variance. Measures to reduce and control the concentrations of TMs in water River of the area, particularly for Cd, Cr and Pb, should be investigated.

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