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Assessing Heavy Metal Contamination In Surface Water And Sediments Of The Tafna River (North-West Of Algeria)

Ouezna Mechouet[1]✉ | AliEddine Foudil Bouras[1] | Noureddine Benaissa[2] | Yasmine Ait Hamadouche[3] | Fatima Zohra Haddad[2] | Alexandru Dimache[4]

1. Geo-environment Laboratory, Faculty of Earth Science, Geography, and Territorial Planning, University of Science and Technology Houari Boumediene (FSTGAT/USTHB), BP 32 El Alia-16000, Alger, Algeria
2. Environmental Monitoring Networks Research Laboratory (LRSE), Faculty of Nature and Life Sciences, University Oran 1, Algeria.
3. Biology of Microorganisms and Biotechnology Laboratory «LBMB», Faculty of Nature and Life Sciences, University Oran 1, Algeria, Department of Biotechnology, Algeria.
4. Ritsumeikan Asia Pacific University College of Asia Pacific Studies Graduate School of Asia Pacific Studies: Ritsumeikan Asia Taiheiyo Daigaku Asia Taiheiyo Gakubu Daigakuin Asia Taiheiyo Kenkyuka

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ABSTRACT

Water and sediments have become a major threat. Heavy metals, some of which are potentially toxic, are distributed in different areas by different routes. Tafna river was studied upstream and downstream under contrasting hydrological conditions during the year 2020.The different levels and sources of pollution are assessed by combining geochemical indicators: geoaccumulation index (GI-go), contamination factor (CF), pollutant loading index (PLI) and supplemented by correlation matrix (CM) as statiscal analyses added principal component analysis (PCA). The elements analysed were physical and chemical parameters (pH, DO, electrical conductivity CE and, COD BOD5), and the metallic elements (Fe, Cd, Pb, Cu, Mn and Zn). They were classified based on how contaminated they were: for the water compartment (Fe> Mn>Cu>Pb>Cd>Zn), while for sediments (Zn> Pb>Fe>Cd>Cu >Mn). The results suggest that the chemical composition of the waters of the Tafna river is influenced by the lithology, which contributes to the enrichment of the sediments. All of the indicators suggest an average levels of sediment and water pollution at the Tafna's summit, then decreases towards the bottom due to the geomorphology with multiple sources of pollution. As a result, our study offers the first comprehensive information on the amount of heavy metals present in the riverbed's sediment and water.

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INTRODUCTION

One of contemporary greatest environmental challenges in these recent years has been the contamination of river, water and sediments, which continues to be dangerous to humans (Bashir et al.,2020). The Major environmental dangers arise from high levels of contaminants in surface waters and sediments (Le Van Muoi et al., 2022). Additionally, both anthropogenic and natural causes will be involved in the accumulating of polluted sediments in waterways. Acknowledging that surface water activities and waste that contain dangerous contaminants have a detrimental impact on human health (Islam, 2021). An essential phase of the hydrosedimentary cycle is the evaluation of trace metals (Rouidi, 2022). Many toxic metals are considered to be transported

*Corresponding Author Email: ouzna23hc@gmail.com

by sediments (Jouanneau et al.,1990) and stored there. (Förstner and Wittman (1981) showed that certain of the heavy metals present in the waters are completely related to the surface sediments.

Therefore, the accumulation of these metallic elements in sediments is not permanent since they can be dumped onto surface waters in answer to changes in the environment's physico-chemical characteristics, especially when the pH is high (Benabdelkader, 2018). These traces of metals could therefore come from two distinct sources: a natural geological source, mainly due to drainage water, erosion and an anthropogenic source resulting from domestic, agricultural and industrial drains. (Rouidi, 2014). They can also be transmitted indirectly, through existing dry and wet discharges as well as agricultural runoff and infiltration (Benjama et al., 2011).

According to (Singh et al., 2005) 99% of pollutants accumulate are locked up in sediments, while only 1% dissolve in water. The increase in anthropisation in recent years has led to a rise in trace elements (Zn, Pb, Fe, Cu, Cd) Wong 2000). Evaluation of metallic elements have been used to assess contamination in waters and sediments (Christian et al.,2020) and contamination indices the CF, PLI and Igo (Tomlinson et al.,1980) having been often utilized (Pena-Icart et al.,2017) to estimate pollution sources, which still represents a major challenge. The pollutant's elements can be can be discharged in the water compartment when the physico-chemical characteristics of the interface between water and sediments are modified as a result disturbances or diffusions; as a result, sediments will become a source of contaminants after being in the well (Ruqayah et al., 2023).

The Tafna is a model of a North African river that flows into semi-arid basins. A study by (Kouidri, 2016) observed that its sediments are polluted with Zn, Cd and Pb. But the fact that little research has assessed the impacts of hydrological conditions and erosion on the transfer of pollution along the wadi to its mouth should also be addressed. According to Taleb et al (2004), the existence of dams on the slopes of the Tafna also has a considerable effect on water quality river. For this project, we measured physico-chemical variables (T°, pH, EC, nitrates, nitrites, and chlorides) both in the field and in the lab (Fe, Al, Cd, Cu, Mn, Pb, and Zn). To better understand the impact and results of anthropophisation on the water quality and sediments along the Tafna river, all the data were submitted to a statistical analysis, beginning with a PCA, to identify a link between the different physico-chemical and metal characteristics.

MATERIAL & METHODS

The Tafna river (Fig.1) is located to the north-west of the Algerian coast and extends as far as Morocco. The Tafna river rises on the hillsides of the Tlemcen mountain, at an altitude of approximately 1,100 metres and flows 170 km from south to north to reach the Mediterranean Sea. The Tafna has a Mediterranean climate (Subarid), with 372 mm of rainfall on average. The hydrological regime is Mediterranean, alternating between a period of storms and another of severe drought; its average annual flow has varied in recent years between (0.11- 0.48) m^3/s (2008-2018 respectively) according to (ANRH 2019). The Tafna is characterized by its bedrock, which is separated into two areas: In the upstream section, the river traverses the canyon which is rich in limestone of Jurassic age, and in the downstream section, which flows a tertiary basin with marl that has recently been filled by Quaternary alluvium (Taleb, 2004) . The presence of four main industrial locations in the area (Tlemcen, Sebdou, Maghnia, and ultimately Oujda) all have anthropogenic activities occurring that will affect the river's water quality

Sampling Protocol and preparation

Three sites along the river (S1, S2, and S3) in the Tafna basin (Fig.1) were collected. The stations have been selected based on findings of earlier research, as a means of assessing the effects on different human activity sources in the studied area. The stations are situated in this

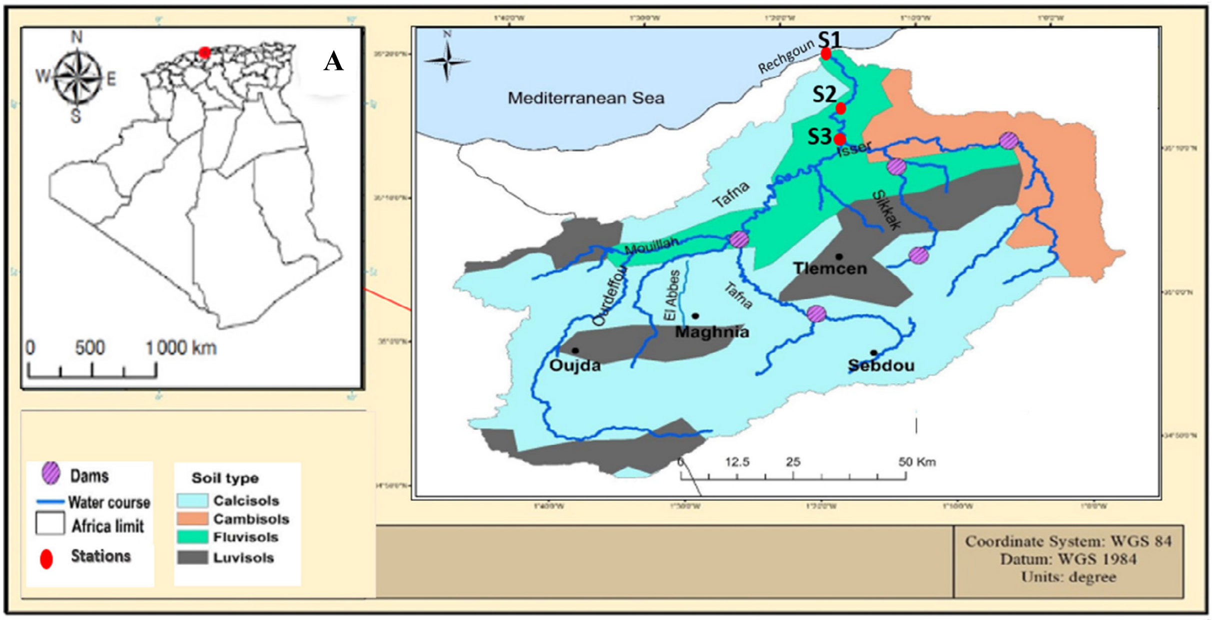

Fig. 1. Representation of study area and sediment-water sampling points in the Tafna River (North-Western Algeria) A: Algeria map; B: Tafna watershed

order: in the downstream of an industrially zoned urban area (S3: 1 km from the mouth), the second close to a public dump and a large flat agricultural area (station S2) which is located at 600m from the S1, Lastly, station 1 (S1: Tafna river's mouth at Rechgoun Beach level) is situated near the Tafna basin's exit. The latter is influenced by sea water. The aqueous samples were taken with a monthly frequency over a period of one year. The samples were carried to the laboratory in a short amount of time, preserved in polyethylene containers, and washed with river water beforehand. Following that, throughout the collection campaigns, both dry and wet, superficial sediments (the sediments were sampled at a depth of between 0 and 10 cm). The samples were air-dried before being cut into quarters, carefully homogenized without crushing and tempered according to AFNOR standards to get the following three fractions (firstly fine fraction <63 µm, one rough fraction (63µm to 2 mm) and in the last a fraction greater than 2 mm). Every portion was measured. Considering it predominates and had a preference for metals, mineralization was carried out on the fraction <63 µm (Probst et al.,1999).

Beginning with surface water samples that were analysed using standard water examination methods (APHA, 1999; Rodier et al., 2009). The electrical conductivity (EC) [Consort 562], pH, and dissolved oxygen (DO)] were among the various physicochemical water parameters that were assessed in situ employing a multiparameter. Measurements of nitrogen and phosphate nutrients and concentrations of major elements and trace metals in water compartments and sediments were carried out using the SAA Agilent 7700X. Standards were used to check the reliability of the analyses. Finaly The DBO mètre OxiTop device was used to evaluate the 5-day biological oxygen demand measurement.

Water and sediment quality assessment

The datasets of surface water of Tafna river and sediment quality parameters were analysed using descriptive statistics [min, max and ±SD, and mean] as the replication was not met for statistical analysis. The spatial variabilities of water quality parameters were compared with the surface water quality guidelines of ALGERIA (JORA, 2011 and the WHO, 2017). Sediment quality parameters were compared with the (WHO, 2017) and another international river having the same properties and with the following pollution indices:

The deterioration of the bottom sediment quality with respect to metal concentrations was assessed based on the geo-accumulation (I-geo) index, which is expressed as follows (Muller 1969)

$$Igeo = log_2\left(\frac{C_n}{1,5*B_n}\right) \quad (1)$$

Where:

C_n is the measured concentration and the geochemical background concentration of metal (n), respectively.

B_n is the geochemical background reference concentration for a metal (n) which is either directly measured in the reference sediments (pre-industrial).

Factor 1.5 is used to account for possible variations in the background data due to lithological changes.

The $Igeo$ values were classified into seven grades as follows: I-geo ≤ 0 (grade 0), unpolluted; 0 < $Igeo$ ≤ 1 (grade 1), slightly polluted; 1 < $Igeo$ ≤ 2 (grade 2), moderately polluted; 2 < $Igeo$ ≤ 3 (grade 3), moderately–severely polluted; 3 < $Igeo$ ≤ 4 (grade 4), severely polluted; 4 < $Igeo$ ≤ 5 (grade 5), severely–extremely polluted; $Igeo$ > 5 (grade 6), extremely polluted.

The pollution load of the sediment for heavy metals was assessed using the contamination factor (C_f), which can be categorized into four grades for monitoring the contamination of a single metal over the study period as follows: low degree (C_f < 1), moderate degree (1 ≤ C_f < 3), substantial degree (3 ≤ C_f < 6), and very high degree (C_f ≥ 6). The CF is expressed as follows (Hakanson 1980):

$$C_f = \frac{C_e}{C_n} \quad (2)$$

Where:

C_e = concentration of the element in the samples of Cn is the concentration of the reference element.

C_n = calculated as the ratio between the metal content in the sediment at a given station and the reference concentrations.

The pollution load index (PLI) was used to determine the mutual pollution effect at different sites. The overall toxicity status of each sampling site was then evaluated based on the PLI. A PLI of 0 indicates excellence, while a PLI of 1 implies the presence of only baseline levels of pollutants. A PLI of > 1 indicates the progressive contamination of the site and estuarine quality. The PLI is expressed as the nth root of the multiplications of the contents (as CF metals) as follows (Tomlinson et al.,1980):

$$PLI = \left(C_{f1} * C_{f2} * C_{f3} * C_{fn} \; .....\right)^{1/n} \quad (3)$$

n: this research, the global mean heavy metal.

Statistical analyzes

The data produced from this study were statistically analyzed using the free statistical software R (R Core Team 2019). The means and standard deviations and inferential statistics (correlation) of heavy metal concentrations in surface water and sediments samples were calculated. Correlation matrix (CM) analysis was used to identify possible significant relationships among heavy metals in surface water and sediment at both 0.01 and 0.05 significant levels. A multivariate method in terms of principal component analysis (PCA) was used to obtain the detailed information of the data-set and gain insight into the distribution of heavy metals by detecting similarities or differences in samples

RESULTS AND DISCUSSION

Spatial variations of water and sediment quality

Surface water quality

Between the rainy (wet) and dry seasons of 2020, Table 1 shows the spatial fluctuation

Table 1. Spatial variability of physicochemical parameters and nutrients, metals elements concentrations among the observed sites in the surface water in the wet and dry seasons of three stations (S1,S2,S3) of Tafna river.

	Station Sample	S1				S2				S3				WHO, 2017
Parameters	Season	**Mean**	**±SD**	**Min**	**Max**	**Mean**	**±SD**	**Min**	**Max**	**Mean**	**±SD**	**Min**	**Max**	
Temperature (°C)	Wet	15,40	3,88	12,7	23	17,6	2,81	14,7	21	17,84	4,50	11	22,8	**25**
	Dry	25,03	3,28	21	29,3	26,0	3,97	21	31	25,35	3,15	20,1	29	
Ph	Wet	8,18	1,17	6,15	9,1	8,1	0,78	7,03	9,1	8,30	0,81	7	9	**6,5<pH<9**
	Dry	8,32	1,39	6,3	10	8,2	1,37	6,6	10	8,25	1,07	6,9	9,7	
EC (us /cm)	Wet	1075,13	681,70	182	1734	883,8	609,6	129	1719	1091,4	520,1	667	2100	**2800**
	Dry	416,00	725,59	69	1892	546,5	613,8	71	71	269,2	331,0	89	1001	
DO (mg/L)	Wet	9,52	1,24	7,88	11	6,5	2,26	5	9,1	4,97	1,21	3,8	6,8	**5<OD<8**
	Dry	11,50	3,84	11	19,1	5,9	1,61	4	8,3	7,41	5,48	2,9	19,1	
DBO$_5$ (mg/L)	Wet	66,97	31,21	30,8	98	74,6	43,32	28,7	143	74,57	43,32	28	143	**5**
	Dry	46,58	18,66	33	82	46,8	14,80	31,1	78	50,95	19,67	30,3	91,7	
COD (mg/L)	Wet	132,00	26,58	42	222	66,8	26,58	22	98	52,00	24,56	23	80	**40**
	Dry	64,83	15,92	44	90	69,8	12,29	56	90	62,17	13,50	49	89	
Ca^{+2} (mg/g)	Wet	66,67	24,56	22,1	90	31,1	5,96	22,5	40,4	31,21	5,91	22,89	40,85	**200**
	Dry	45,12	14,86	17,4	60,3	45,4	15,85	15,8	60,41	45,69	17,54	13	65	
SO4^{-2} (mg/L)	Wet	1,23	0,64	0,51	2,01	1,2	0,48	0,82	2	1,38	0,59	0,638	2,06	**400**
	Dry	2,65	0,86	1,10	3,66	3,0	1,41	1,20	5,02	3,63	1,97	1,35	6,28	
NO$_2^-$ (mg/L)	Wet	0,73	0,54	0,05	1,29	0,5	0,51	0,04	0,516	0,52	0,53	0,01	1,19	**50**
	Dry	0,40	0,36	0,06	0,91	0,5	0,34	0,09	0,9	0,42	0,34	0,061	0,9	
NO$_3^-$ (mg/L)	Wet	0,05	0,05	0,01	0,13	0,1	0,16	0,01	0,431	0,08	0,10	0,011	0,27	**0,2**
	Dry	0,08	0,06	0	0,16	0,1	0,08	0,01	0,2	0,10	0,089	0,012	0,22	
NH$_4^+$ mg/L)	Wet	0,04	0,03	0,02	0,08	0,05	0,02	0,04	0,081	0,06	0,02	0,019	0,08	**0,7**
	Dry	0,11	0,12	0,02	0,37	0,04	0,02	0	0,058	0,03	0,02	0,007	0,056	
PO$_3$O$_4$- mg/L)	Wet	1,01	0,50	0,21	1,6	0,9	0,41	0,51	1,65	0,77	0,48	0,15	1,55	**5**
	Dry	0,74	0,40	0,17	1,41	1,0	0,38	0,61	1,79	1,00	0,41	0,6	1,87	
Fe^{+2} (µg/L)	Wet	32,45	37,38	0,62	90	29,2	36,36	0,51	90	41,74	50,93	0,66	110	**0,3**
	Dry	0,81	0,63	0,12	1,8	0,8	0,51	0,18	1,7	1,07	0,42	0,56	1,8	
Cu^{+2} (µg/L)	Wet	1,61	0,52	1	2,2	0,9	0,53	0,05	1,7	0,97	0,55	0,09	1,61	**2**
	Dry	1,08	0,46	0,73	1,88	1,6	0,87	0,78	3	1,17	0,51	0,73	1,99	
Cd^{+2} (µg/L)	Wet	0,30	0,23	0,12	0,76	0,3	0,26	0,03	0,66	0,53	0,36	0,2	0,98	**3**
	Dry	1,02	0,83	0,06	2,1	2,2	1,48	0,04	3,99	1,94	0,99	0,71	3,4	
Pb^{+2} (µg/L)	Wet	0,95	1,34	0,02	3,52	1,4	1,55	0,1	4,33	0,75	0,83	0,02	2	**10**
	Dry	1,59	0,74	0,85	2,71	1,9	0,39	1,31	2,4	1,30	1,30	0,5	2,01	
Zn^{+2} (µg/L)	Wet	1,64	0,56	0,61	2,51	1,4	0,63	0,22	2,11	1,49	0,74	0,4	2,41	**5**
	Dry	3,39	1,54	1	5,11	3,8	1,33	1,3	6,11	4,13	2,21	1	6,71	
Mn (µg/L)	Wet	35,01	28,57	0,02	70	50,0	49,99	0,02	100	47,51	0,00	0,01	95	-
	Dry	33,01	26,94	0,01	66	64,5	64,50	0,01	129	58,01	0,00	0,01	116	

water quality measurements throughout the monitored stations. These analyses were aimed at understanding the influence of natural and anthropic contributions in the composition of the wadi waters and their origins. The water temperature varied just slightly between the sample locations throughout each season, but it was greater during the dry season (23°C to 27°C, $\overline{x}$= 25°C) than the wet period (11°C to 19°C, $\overline{x}$= 14°C) this variation could be explained by the climatic conditions, this variation is very near to the range observed in the Moroccan river Sebou (Perrin et al., 2014). The observed pH values similarly exhibited low regional variation in both seasons, which may be attributed to the direct influence of salty water, but also possessed alkaline characteristics (pH: $\overline{x}$ =8.1), in the dry season often corresponds to high temperatures (Table 1), favoring the precipitation of calcite and therefore the decrease of the pH. It can be explained by the fact that the Tafna river drains mainly calcareous soils and rocks. In general, the pH variations were above the parameters suggested by the (WHO 2017) for acceptable water quality.

EC varies from one station to another and according to the periods. This parameter, which depends on temperature and mineralization, having a mean value of 1120.43 µS /cm, that's lower than the global standards of 1500 µS /cm (WHO, 2017) and (2800 µS /cm) references (JORA, 2011) showed in (Table 1). It is still high, though, as natural waters typically vary from 50 to 1500 µs /cm (Loucif et al., 2020; WHO, 2017). Their averages vary between $\overline{x}$=1080 µs/cm in dry period and $\overline{x}$ = 1159 µs/cm in wet period (Table 1). According to (Benabdelkader, 2018), these contents could be explained by the releasing of mineral salts from agricultural present in the Tafna soils, at the time the dissolve of particular mineral elements that come from the sediments related to the aquifer, as well as to the mineralization of organic substances produced by the industries present in the area and public dumps, waste water directly entering the groundwater by water infiltration.

In surface water, dissolved oxygen (OD) is essential factor, due to how it impacts the maintenance of aquatic life and the self-purification of water (Haritash et al., 2016; Kumar et al., 2018), The concentration of DO in the current research was 8.35 mg/L; this result is well under the WHO 2017 guidelines of (5-8 mg/L) in (Table1).

The higher values of Dissolved Oxygen OD is remarkable between the seasons Dry $\overline{x}$= 8.2 mg/L and $\overline{x}$=6,7 mg/L in wet, when it's dry, this parameter is bigger than when it's wet. Because during the dry period the temperatures are high and less precipitation according to (ANRH, 2015) will lead to a depletion of wadi water in oxygen and favoring the intense respiration of the biocenosis.

The BOD_5 (The 5-day biological Oxygen Demand) and COD (COD: Chemical Oxygen Demand) reflect the amount of organic matter soluble in water, this quantity present in the river is 29.12 mg/L, is higher than the oxygen value necessary for microorganisms to degrade the organic matter threshold value set by the WHO (2017), measured oscillate from [25.2 to 58.3 mg/L] (Table 1) presenting a very strong correlation between the two parameters with a coefficient R^2 = 0. 87 (Fig.2), indicating a slight pollution because according to (Rodier 2009) beyond 25 mg/L, a water pollution by fertilizers is reported. The variance in DCO concentration between the S1 and S3 embouchures decreases from 52 to 132 mg/L during the wet period (Table 1), indicating the discharge of domestic waste water and industrial unit effluents as well as the presence of organic material that is biodegradable. Concentrations of eutrophic substances (PO_4^{3-} and NO^{3-}, NO^{2-}, NH_4^+) (Fig.3) vary from one substance to another. According to Rejsek (2002) and Rodier et al., (2009), nitrate concentrations in unpolluted natural waterways vary from 1 to 15 mg/L depending on the season and the source of the water.

A concentration of 2 to 3 mg/L is regarded as typical, despite direct effluent discharges from existing agricultural and industrial practices on both banks. Given the weak redox conditions in the water column and the predominance of nitrification operations in nitrogen N trends, the lack of nutrients might be attributed to these conditions (Benabdelkader, 2018).The low

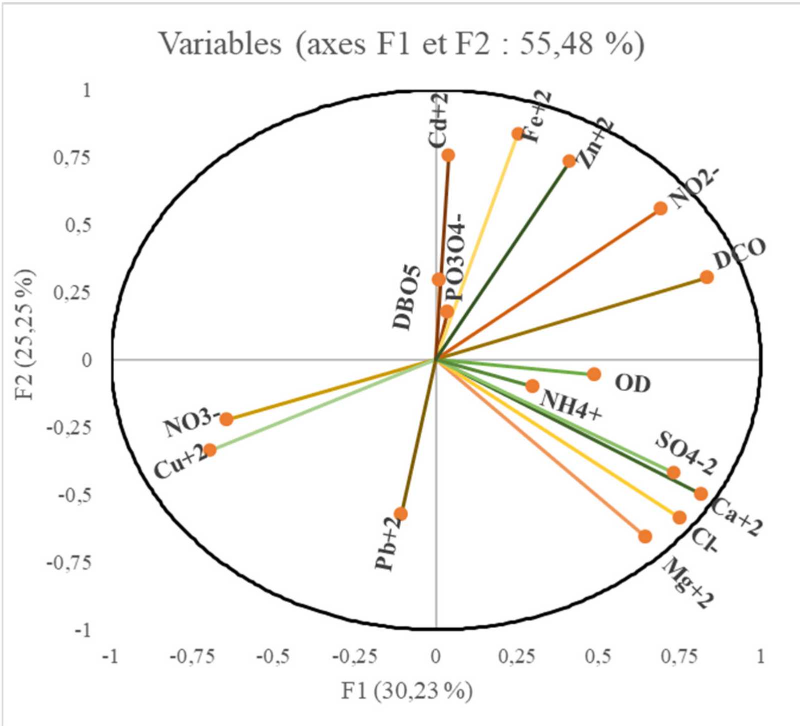

Fig. 2. PCA based on heavy metal concentrations for the Tafna waters located in 2018

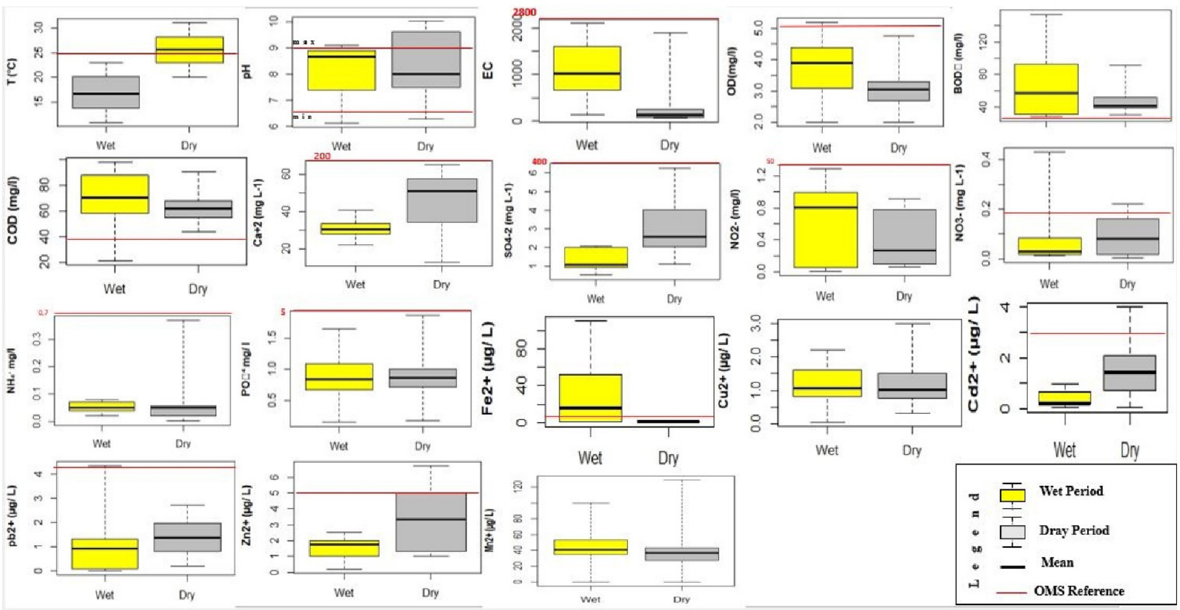

Fig. 3. Spatial variation of the physicochemical and metallics parameters of surface water collected at Tafna river, northeastern Algeria. The values displayed are the mean (solid grey circle) ± SD (vertical bars). These graphs are a function of the seasonal [Dry and Wet]

concentration of N-NH_4^+ where its variations are [$\overline{x}$=0.5 mg/L] (Table 1**)** is probably because alkaline water's pH (more than 7.0) affects the majority of stations and seasons. According to previous research (Taleb et al., 2004), NH4+ is highly dependent on pH and is elevated in an acid aquatic environment (pH is low then 7.0).

Similar to this, the phosphate level in the Tafna, [x=0.3mg/L], was not elevated over the suggested threshold of 5 mg/L by Rodier et al., (2009) and (WHO, 2017) (Table 1).The properties of the Tafna's traversing areas and the breakdown of organic materials are closely connected to its natural presence in water (Kumar et al., 2018). In contrast, the concentrations of nitrogen particles N found in the same sample sites over the course of the two seasons are much higher than those of phosphates P examined in this study. However the research of Taleb (2004) and Bouzid (2008) indicates that the existence of the dam as well as the industrial waste, which was removed in 2014, caused the phosphorus P extra to be truly very high in the water of the S3 (Fig.1) of the Tafna river.Metal elements measured at all sample locations demonstrate that some are considerably below WHO water quality guidelines (WHO, 2017). The results were collected during our field study in the Tafna region (Table 1). As a result, agricultural and industrial activities (such as factories and ENOF) have a major effect on the studied region. Nonetheless, the modest quantities of metals observed might be attributed to physicochemical processes occurring in the riparian habitat. There concentrations of (Cd, Zn ,Cu, Fe, Pb and Mn) in waters of the Tafna are in the following order of importance Fe>Mn>Cu>Pb>Cd<Zn. They are in the range of concentrations of natural rivers of the world (CNRM, Meybeck and Helmer 1989) for Cd and Pb, as opposed to the normal amounts of Cu and Zn and Fe are higher. The average concentrations of the Tafna River exceed those observed by Koukal et al., (2004) for the Sebou River (watershed located in Morocco). These concentrations of Fe and Mn are relatively high in relation to the presence of clay minerals (kaolinite and illite) (Charuseiam et al., 2022), which are enriched in these elements in the formations drained by the Tafna (Benabdelkader, 2018).

In order to identify the sources of pollution in the surface waters of the Tafna, the (Fig 2) present a multivariate analysis through the PCA carried out on a double entry table (16 variables on 3 stations). We were able to establish a relationship between the various physico-chemical and metallic parameters and better assess the effect of human activities on the water quality of Oued Tafna. The projection of the variables onto the F1 and F2 factorial planes shows two poles (Fig 2): F1, which accounts for 30.23% of the variance, expresses an axis characterising the mineralization of the water by the leaching of geological formations, and is determined by ortho-phosphates, cadmium, zinc, iron, sulphates, temperature, chlorides, COD and Calcium. Factor plane F2, which represents only 25.25% of the information, is considered to be an axis characterising agricultural pollution and is determined by nitrates and lead and copper ions (Fig 3). The high loads for DO, NH_4^+, BOD_5^-, Ca^{2+} and Cl^- were probably mainly influenced by discharges from uncontrolled agricultural activities, which explains the high COD content. The high negative loads for $N\text{-}NO_3^-$ in both seasons (Fig 3) could be related to high pH levels and salinity. Therefore, the low content and narrow variation of N compounds in coastal areas are due to the effects of high salinity levels (Dauda et al., 2019). These PCA results obtained, we notice many very significant correlations have been identified between all the variables measured and the contribution of phosphate ions is however quite negligible compared to the measurement of all the other elements that present correlations more or less strong in relation to each other.

Sediment quality

Table 2 shows the spatial fluctuations of river sediment characteristics at the studied stations throughout both wet and dry seasons. Because the readings of pH had been moderately acidic, these values were lower than those measured in water's surface at the same locations S1, S2, S3, most likely due to decomposing of stored organic substances derived from drained water, which could be related to the existence of acid humic created about breaking down organic substances and an acidic sulfates sediment (Benabdelkader et al., 2018).

Table 2. Mean ($\overline{x}$) concentrations of trace metals and major elements in sediments collected during the both sampling periods Dry and Wet (n=40, except) at each sampling station of the Tafna River. Comparison of the results obtained with the other rivers of the world from 2005-2022

		Tafna (Northwest - Algeria)	**Ca Mau Peninsular (Vietnam)**	**Saf-Saf (Northest - Algeria)**	**Suches (Peru)**	**Tafna (Algeria)**	**Bou Regreg (Maroc)**	**Tafna (Algeria)**	**Lukkos (Maroc)**	**Sebou (Maroc)**
	Parametre	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
Physico-chimical elmts	**Ph**	7,1	7,72	7,58	-	7,1	7,7	7,2	7	7,4
	CE	658,5	137,76	-	-	-	3430	780,6	-	-
Major elmts (mg/g)	**Ca**	102,6	100	10,790	-	100	-	-	-	90
	Al	30,1	-	-	11604,4	-	-	-	-	53,450
	Fe	16,1	9	199,5	28609,000	-	61,000	15,38	31,06	29,200
	Mg	13,8	9,240		-	-	-	-	-	12,780
	Mn	0,6		402,210	291,720	-	-	410,83	-	5,790
Traces Metals (µg\L)	**Cu**	13,5	18,210	36,360	-	17,51	21	42,97	22,8	51,500
	Zn	59,0	39,480	62,66	63,9	74,31	-	338,7	115,97	179,000
	pb	14,8	12,210	-	41,4	43,37	17	52,73	102,9	
	Cd	1,8	-	12,080	12,540	0,19	2,900	3,4	-	-
Reference		**MECHOUET et al., 2019-2020**	**Le Van Muoi, 2022**	**Rouidi ,2022**	**Dante Salas ,2022**	**Benabdelkader , 2016**	**Nadem et al., 2015**	**Trari, 2015**	**El Morhit et al., 2008**	**Cheggour et al., 2005**

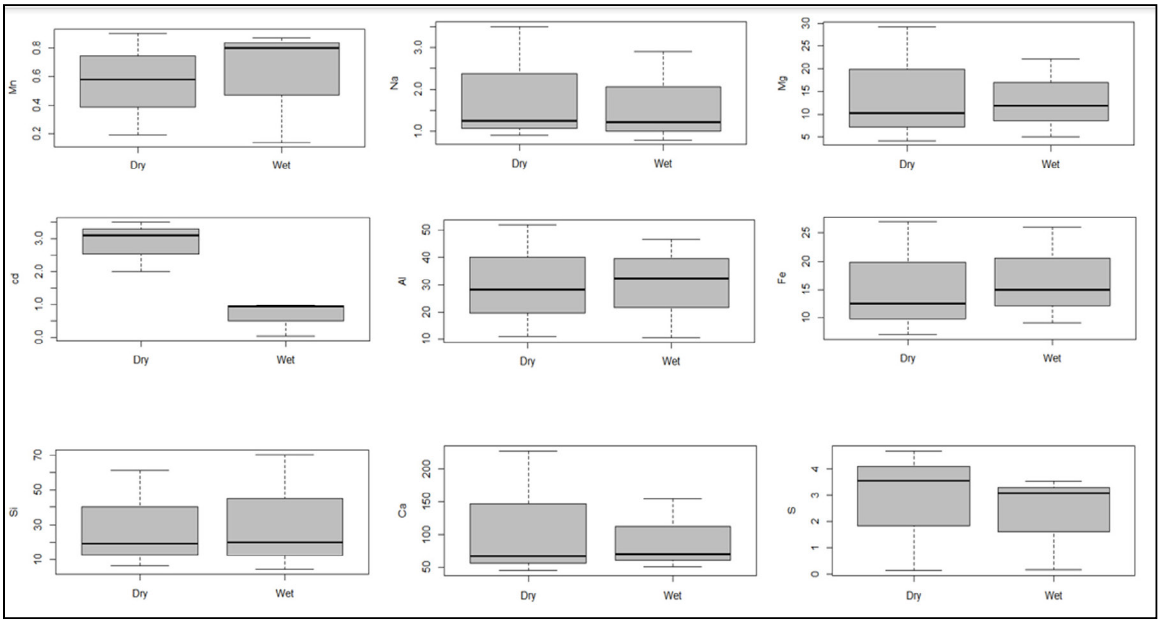

Fig. 4. Spatial variation of the physicochemical and metalics parameters of sediment collected at Tafna river, northeastern Algeria. The values displayed are the mean (solid grey circle) ± SD (vertical bars). these graphs are a function of the seasonal [Dry and Wet]

The findings produced and represented (Fig.4) demonstrate that the chemical composition of the sediments with a Fine fraction <63µm in major and metallic elements follows the following classification: (Zn >Pb>Cu> Cu >Cd). It is noted that the concentration of Calcium is the most abundant in the sediments of Tafna comparing to those rivers of the world, its average oscillates between the two seasons in ($\overline{x}$=102.62 - 100.54 mg/g), indicating the carbonate characteristic of the slope of Tafna as was shown by (Benabdelkader, 2018). This distribution is controlled by the texture of the sediments with the affinity of cations and carbonates (Fig.4) for fine particles from the weathering processes of primary rock minerals into secondary minerals (Belhadj, 2002).

The analysis of TMEs show that the The mean concentration of trace metals found in sediments was in the order of : Zn > Pb > Cd > Cu. this concentrations are able to be contrasted with the amounts found in different rivers that drain in the Mediterranean Sea (Table 2). However, the concentrations were greater for Pb, Zn, Cd, and Cu compared to the Sebou river's (El Azhari et al., 2016). These metal elements are distributed according to the order of the stations following S1>S2>S3. Their concentrations vary between 0.81 µg.g^{-1} in Cd and 22.31 µg. g^{-1} in Pb, and 0.15 µg. g-1 and 41.40 µg. g^{-1} in Zn, they are higher than those amid the bottom sediments Moulouya's river based in Morocco royaum, and it is also noted that a very large difference was found in the same study area between 2015 and 2019 for the elements (Cu, Zn, Pb) where their values really exceeded the WHO standards, 2011 this is due to the presence of an untreated wastewater discharge directly to the wadi. The concentration of lead was exceptionally variable, as reflected by the usual deviation from the average. They are influenced by natural processes of alteration as well as anthropic contributions, due to the punctual discharges of domestic waste, or agricultural fertilizers used inconsiderately by the lack , of know-how that will subsequently degrade the aquatic biotope and put it in potential danger.

With a view to establish relationships between metals and verify the similarity of their sources in the Tafna estuary's surface sediments, a bi-variate linear correlation study between the parameters studied (Table 3) was carried out to provide information on the strength of

Table 3. Correlation matrix between major and trace metal elements in Tafna sediments

	Mn	Fe	Cd	Cu	Zn	Pb
Mn	1					
Fe	0.88	1				
Cd	0,25	0,23	1			
Cu	0,73	0,71	-0,2	1		
Zn	0,89	0,90	0,3	0,78	1	
Pb	0,90	0,99	0,2	0,8	0,9	1

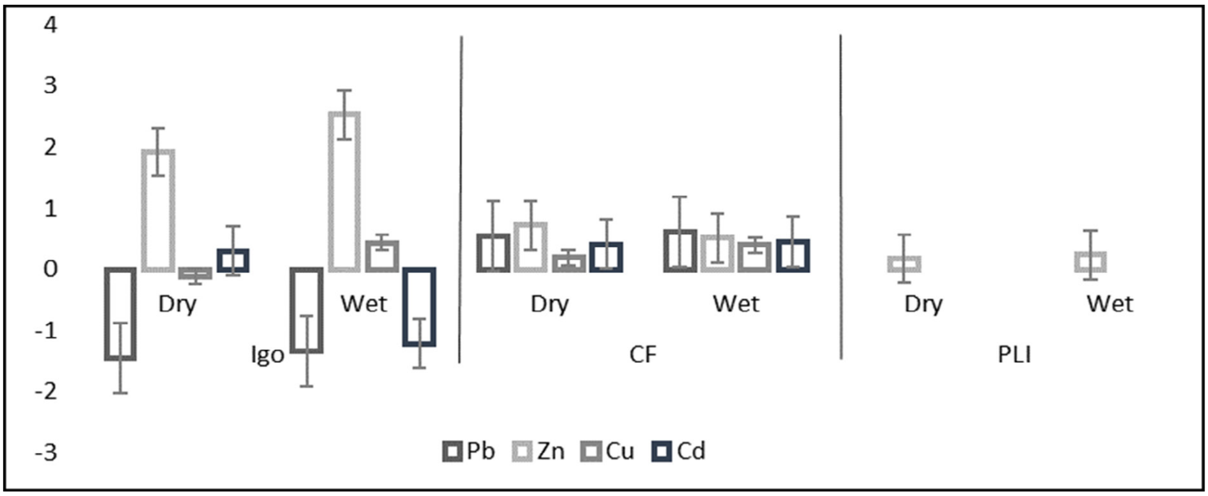

Fig. 6. Index values (I-geo, CF, and PLI) of heavy metals in surface sediment of Tafna river. Number of samples for calculating the index values (for the heavy metals in the wet and dry seasons)

any associations between them. According to the Pearson correlation coefficients presented in (Table 3). A significant positive correlation exists between the metallic elements Fe, Mn and Pb ($0.83< r <0.88$, $p<0.05$) illustred in (Table 3). As well as among Fe and Zn ($r = 0.96$, $n =10$, $p<0.05$). This clear and strong correlation indicates that these elements are the result of anthropogenic activities, namely riverside urban discharges and industrial discharges, which have already been reported in articles by (Taleb, 2014 and Benabdelkader, 2018).

According to a literature review, the presence of a former mining operation (El Abed) located on the border between Algeria and Morocco may be an origin of Zn , Pb in the Tafna basin (Uddin and Jeong, 2021). Hydrology also has an influence on the enrichment of TMEs in sediments. Cd, Zn and Cu are enriched more in wet periods than in dry periods by dilution processes.

Various contamination indicators were hired to analyze the metals enrichment of Tafna river sediments as a result (Siddiqui, 2019) from humans' activities which are summarized as: the Geo Accumulation Index (Muller, 1969), CF and The PLI (Singh, 2005). The aim was for them to use their various abilities to detect pollution in the Tafna River and to discuss their strengths and flaws. The results of these quantitative indices are illustred in (Fig.6). The PLI scores obtained are < 1, indicating that the river surface sediments were not polluted with metals. All metals had CF values < 1, indicating a low level of contamination in dry and rainy seasons. Zn levels at various dry season locations were consistent with a moderate amount of contamination ($1 \leq CF < 3$). In general, dry season CF values were classified as Zn > Pb > Cd > Cu, while wet season CF values were classified as Pb > Zn > Cd > Cu. The I-geo readings in (Fig.6) showed negatives results for the Pb, Cu, and Cd, suggesting uncontaminated sediments and low background levels of these metals. In the dry season I-geo values ranged as Zn < Cd< Cu< Pb, whereas in wet season the I-geo levels varied from Zn < Cu < Cd < Pb.

CONCLUSION

In accordance with findings of this study, the identification of sources and processes of mobilization of physicochemical parameters and heavy metals in surface waters and sediments of the river Tafna was made. The sediments were found to be significantly enriched in zinc and cadmium.

The PCA and PLI clearly demonstrated that the necessary and harmful components originated from anthropogenic and natural sources, respectively. and for the I-geo findings of the two dry seasons, the metals were categorized as follows by concentrations in the environment investigated (Zn Cd Cu Pb), whereas the metals in the rainy season were classed as Zn Cu Cd Pb. This high index, which allowed the locations to be ranked in order of pollution, is not always a good thing. This study shows that integrated features, such as the identification of heavy metals in aquatic water bodies and their distribution, as well as the way they contribute to accumulating in the human body via various exposure pathways, might be investigated in the future

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors

LIFE SCIENCE REPORTING

No life science threat was practiced in this research

AUTHOR CONTRIBUTION

Ouezna MECHOUET [1] and AliEddine FOUDIL BOURAS: Collected sample water from Tafna river, elaboring methodology, data collection and article writing and Prof Noureddine BENAISSA: supervision, sampling, methodology, data collection , Fatima Zohra HADDAD and Yasmine Ait HAMADOUCHE: visualization and revision of the article. Finaly Alexandru DIMACHE: Statistical analyses and revision of the article. All authors reviewed and approved this manuscript.

ABBREVIATIONS

ANRH: National Agency for Hydrological Resources
Al: Aluminium
Cd: Cadimium
CF: Contamination Factor
Cu: Copper
COD: Chemical Oxygen Demand ***DO:*** Dissolved Oxygen
EC: Electrical Conductivity
Fe: Iron
I-Geo: Index of Geoaccumulation
JORA: Official Journal of the Algerian Republic
Max: maximum
Min: minimum
Mn: Mangnesium
Pb: Lead
PCA: Principal Component Analysis
PLI: Pollution Load Index
SAA: Spectrophotometry Adsoption Atomic
SD: Standard Deviation
T: Temperature
TME :Trace metal elements
Zn: Zinc

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