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Assessment of Heavy Metals in the Sediments of the Inaouene Watershed Upstream the Idriss 1st Dam, Northern Morocco

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ABSTRACT

In order to evaluate the degree of sediment contamination by metallic trace elements in the watershed of Oued Inaouene (North-East of Morocco), samples of surface sediments were taken along the river and at the level of the Idriss 1st dam. The objective was to obtain thorough knowledge of the environment (metallic element content, organic matter content, granulometry, and pH, EC, $CaCO_3$ content) in order to identify the degree of pollution in these sediments. The results of analysis have highlighted a contamination accentuated by Ba, Sr, P, Cu, Pb, In fact, this element is present at very high levels, with a maximum content ppm for the samples taken upstream of Oued Inaouene. This increase is related to the physicochemical conditions of the environment, despite the diversity of sources of pollutants. The analysis of hazardous heavy metals showed the values under the detection limits. The qualitative study allowed to identifying the source of contamination, it is an anthropogenic source related to the discharges of cities in vicinity of Oued Inaouene, and natural considered as the main source of pollution by trace elements of sediments that constitute an important reserve of pollutants in the environment

Keywords: sediments, metallic trace elements, Inaouene River, Idriss 1st dam, pollution.

INTRODUCTION

Despite the studies conducted in the Sebou watershed on water quality, little attention has been paid to the water quality of the Inaouene River and especially the concentration of trace elements in its various compartments. The available documentation concerning this subject is rare or scattered and consequently, the need to study in a more precise and concrete way the presence of trace elements in the various studied compartments.

Therefore, the determination of the content of these elements, specifically in sediments, is a way to determine the impact of pollution of waterways, whether natural or due to anthropogenic activity. Sediments act as reservoirs of heavy metals (Zhang et al., 2016), which can be transferred and transported in part to water.

Knowing that in the aquatic system the mobilization of heavy metals is fast, some of these pollutants can be accumulated in the sediment biotope. Adsorption of metals is occurs on inorganic and organic particles. They are incorporated in the accumulated sediments, which results in increased heavy metal contents in them (Ochieng et al., 2007).

Upon a change in environmental conditions, such as (bioturbation, redox potential, organic matter, pH, and other conditions), heavy metals are not permanently fixed, but they can be released into the water column (Superville et al, 2014); as a result, the environmental safety of water will be threatened, creating a health hazard for living organisms (Xu et al., 2017).

Natural aquatic ecosystems are characterized by low concentrations of heavy metals, generally in the nanogram or microgram per liter range (Abubakar et al., 2015). After infiltrating into the aquatic environment via various sources, they mainly come from agricultural runoff, substrate alteration, wastewater and atmospheric deposition (Guo et al., 2018).

By contrast to other pollutants, such as petroleum-derived hydrocarbons and organic pollutants that can be decomposed during natural processes, heavy metals accumulate discretely, and subsequently reach toxic thresholds in the environment (Changbing et al., 2008).

The watershed of the Inaouene River has known a relatively low industrial activity; on the other hand, during the last years it has undergone a very important agricultural extension and a significant demographic evolution. This contributes mainly to the pollution of the river, which recovers all the waste and wastewater discharged by the various cities and villages located along its path and that did not have a previous treatment, thus influencing its physico-chemical quality (Laaraj et al., 2020).

In fact, the dam of Idriss 1st which is considered one of the largest dams in Morocco in terms of capacity and storage, receives water from its main stream of Inaouene. Hence, the need to recover the sediments in order to determine the quality of Oued Inaouene, and the dam, as well as to understand the process of exchange between compartment water - sediments, with the aim of identifying the points that will have a harmful effect and that require urgent treatment.

Presentation of study area

The watersheds of Inaouene (Fig. 1) are located in northern Morocco in the eastern most part of the Saïss basin, depending on the region of Fes-Taza. It is situated between the parallels (33.84N; 34.58N) and the meridians (3.78W; 4.91W), limited to the north by the Pre-Rif and the south by the Middle Atlas, to the east by the

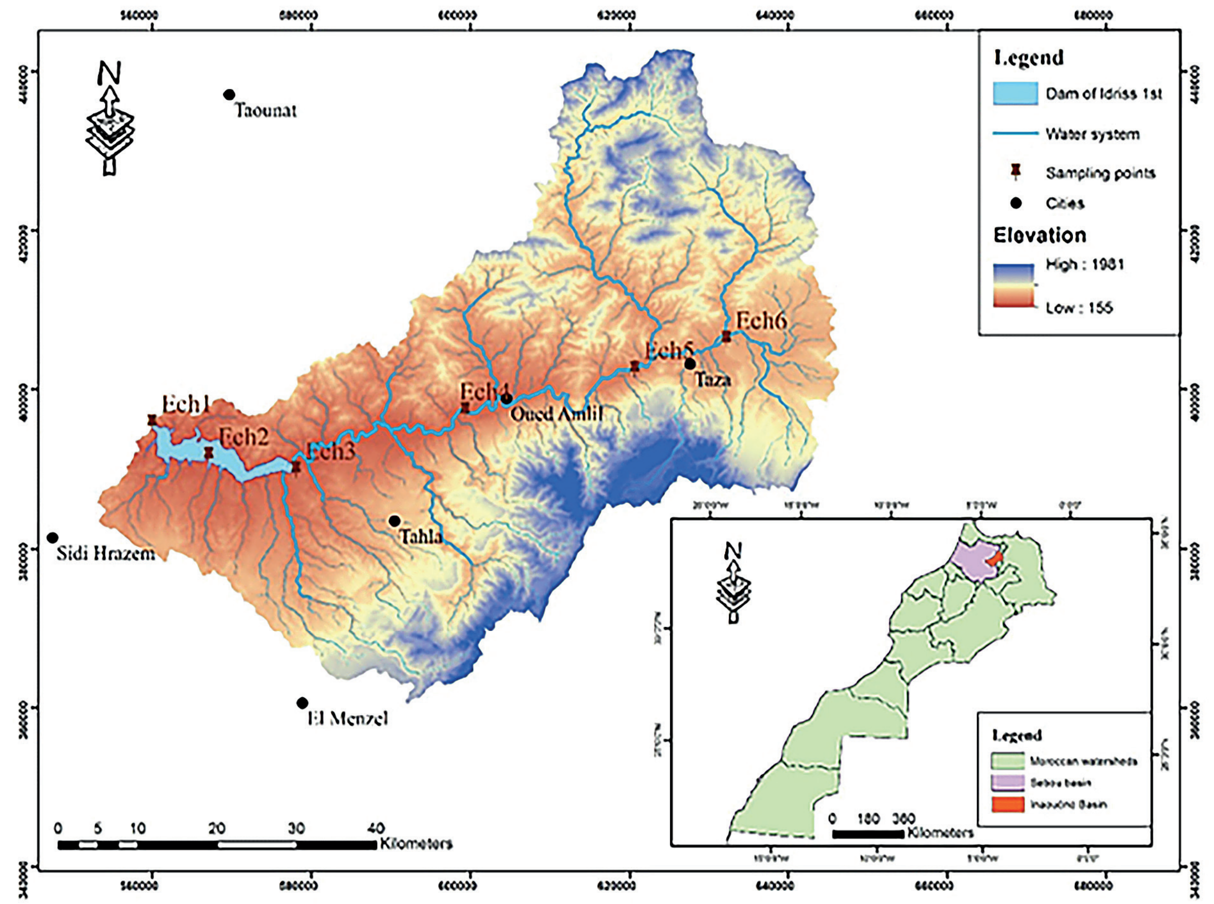


Figure 1. Location of the study area and sampling sites

Middle Moulouya, to the north-west by the Upper Ouergha and to the south-west by the Upper Sebou. The climate, which is determined by geomorphological characteristics, is semi-arid, cold in winter and hot in summer.

The watershed is subdivided into three structural domains, in the north, the hills of the Pre-Rif, while in the south stand the mountains of the northern Middle Atlas and the Paleozoic massif of Tazekka (Mesrar, 2013) (Fig. 2). The soil coverage of the basin is proportional to the lithology. This coverage can be represented by two main varieties of soil: thin soils that cover the highlands of the Pre-Rif and Middle Atlas opposed by thick soils that cover the lowlands as the river terraces of Inaouene (Naoura, 2012). The vegetation cover develops in the north-east and south of the basin, these two factors influence the hydrographic network, which is more important on the north bank than on the south bank. The direction of flow of Oued Inaouene is from east to west over a distance of 163.5 km, from the confluence of Oued Larbae and Oued Lahdar to the confluence with Oued Sebou, the source of water at the basin is of high quality (Naoura, 2012). Thereafter, when it crosses the city of Taza, the quality of Oued Amlil becomes poor due to discharge.

MATERIALS AND METHODS

Sediment sampling and analysis

The six sampling points were selected taking into account domestic discharges, runoff and inputs from the Inaouene river, as well as the locations where the presence of contaminants is suspected or on the most sensitive points of the basin. The sampling was conducted during the dry season over 2 years namely 10th June 2018, and 4th June 2019. The sediment sampling sites are materialized on the map in Figure 1.

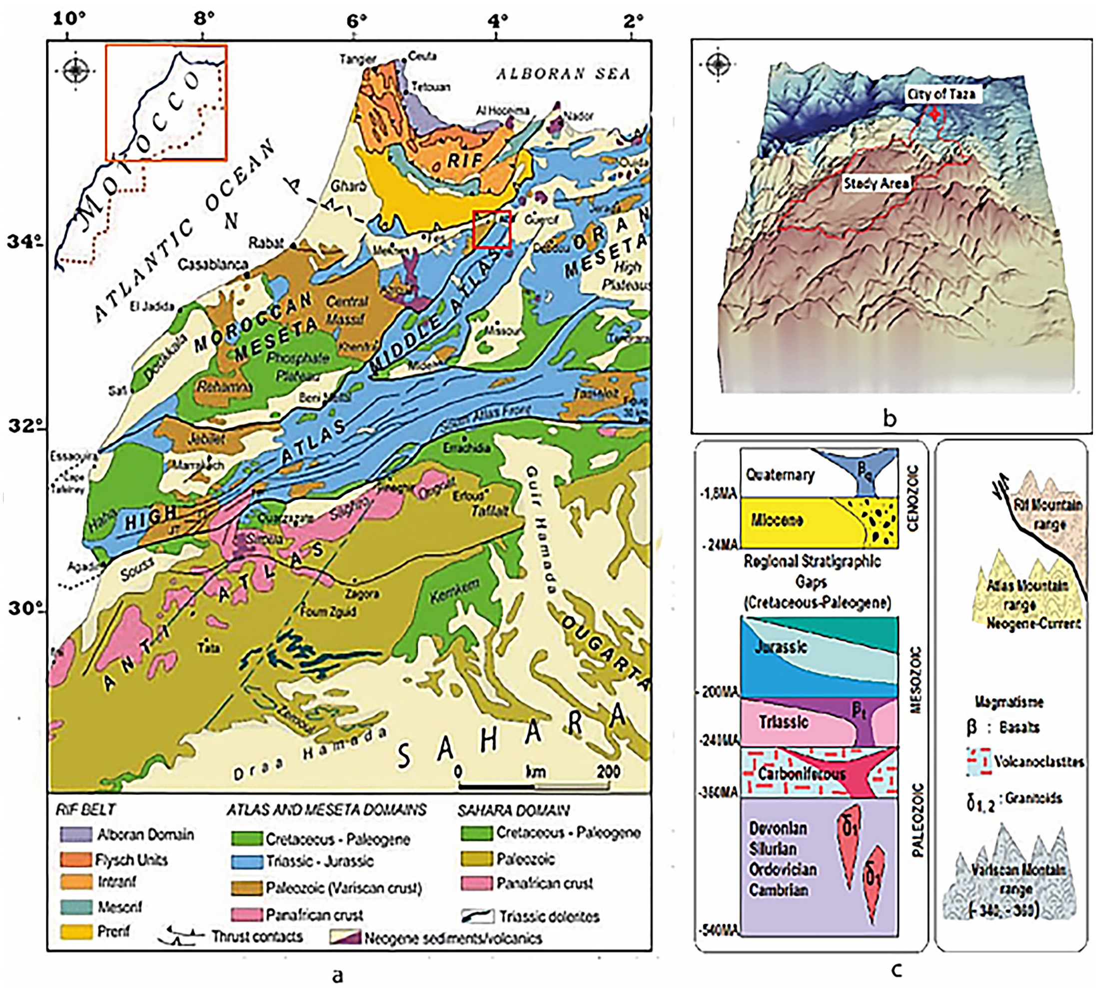


Figure 2. Location map and characteristics of the study area; a) location map of the study area (modified after (Frizon de Lamotte et al., 2004); b) MNT of the study area; c) Stratigraphy and paleogeography of the study area

The sediments were sieved to a diameter of <5mm and then placed in plastic bags that were carefully sealed to avoid contact with air. They are kept in a cold room at a temperature of 4°C in order to minimize any bacterial activity that could modify their properties.

The AFNOR standards on "Soil Quality" (AFNOR 1994) were used for most of the physico-chemical analyses. This choice was motivated by the similarities in composition and physicochemical characteristics between soils and sediments. Thus, the NF X31-101 standard is used in order to have a representative fraction of the raw sample for the experiments, as it is described in detail in a previous study (Wang et al., 2017). This standard consists in drying the sample in the oven under a temperature of 40°C until the mass is constant. This step is followed by clod reduction and sieving of the sample to an average diameter of 2 mm. Thus, all physico-chemical analyses will be conducted with the samples prepared in this way.

The pH expresses the real acidity and takes into account the free H_3O^+ ions in the liquid phase. This measurement is described by the NF X 31-103 standard, while the standard used to determine the value of electrical conductivity is the NF X 31-113, which is based on the extraction of salts from a water soluble sample. The determination of limestone by the method of Calcimetry of Bernard was according to the NF P18-508 standard.

The rate of total organic matter present in the sediments was analyzed by using the method of loss on ignition. The granulometric analysis by sieving is carried out by sieving under water (wet way), according to the AFNOR standard (XP P 94 041). On the other hand, the NF X 31 151 standard is used to describe the solution of trace metal elements, by attack with HF/HNO_3 acids. The concentration of heavy metals was determined by Coupled Plasma Spectrometry (ICP-AES) in the laboratory of the National Office of Hydrocarbons and Mines (ONHYM).

Statistical analysis

The multifactorial analysis (PCA) which was made by the XLSTAT software, allowed classifying and processing the information related to the metallic trace elements in the sediments during the sampling campaigns during the two years 2018 and 2019 by the establishment of the correlations between all the variables of Oued Inaouene. This PCA is performed on a data matrix consisting of 10 samples (6 stations, 2 periods) during which the 13 variables (P, Zn, Cu, Sr, Ni, pH, M.o etc.) were measured.

RESULTS AND DISCUSSIONS

Physico-chemical characteristics of sediments

The pH variation is the factor the effect of which on the mobility of metals is the most determining. The pH measured is alkaline in majority (Fig. 3a) with the values that range between 7.5 and 8.5 this shows that these sediments remain influenced by limestone. Samples Ech2, Ech3, Ech4, Ech5 and Ech6 are of medium alkalinity with a pH value between 8.0 and 8.5, with the exception of sample Ech1 which has low alkalinity recorded in 2019; therefore, a slight decrease in pH which mainly is due to the evaporation of water, generating enrichment in dissolved elements. On the other hand, it also results from the dissociation of the molecule of water releasing hydrogen ions in the environment, which results in the acidification of the environment. According to Bonnet (2000), the pH is strongly linked to carbonates and bicarbonates, in fact, the sediments studied are rich in carbonates, the latter coming essentially from the erosion of the geochemical background constituted by marl and dolomitic formations of the Miocene and limestone rich in carbonates. This favors the contamination of sediments. Indeed, according to Gharbi (2008), the increase of pH contributes to the decrease of the surface potential, by decreasing the competition of protons with respect to metal ions, which favors their fixation, precipitation can also occur at high pH.

Trace metal elements (TMEs) can be mobilized when environmental conditions change, especially pH, according to Quantin (2001), when pH decreases, desorption or dissolution processes will tend to lead to the release of metal cations from the sediment to the dissolved phase, while a prevailing alkaline pH in Oued Inaouene favors the precipitation of metals and their complexes.

The results of conductivity measurements are shown in Figure 3b, the measured conductivities are higher in 2019 compared to 2018; moreover, significant values are notice upstream of the Inaouene watershed and begin to decrease towards the Idriss 1st dam.

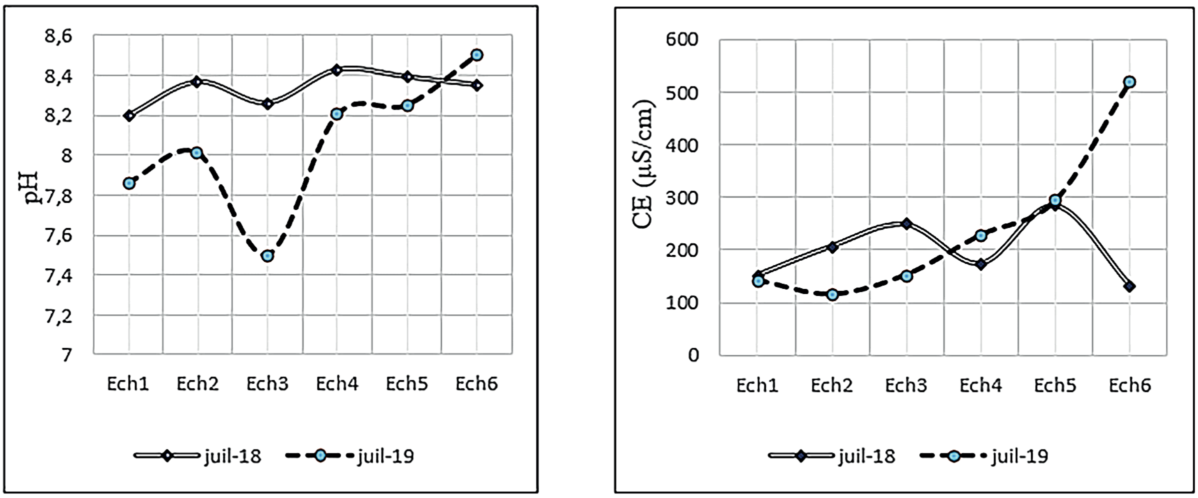


Figure 3. a) Spatial variation of pH and b) electrical conductivity in the sediments of River Inaouéne, Idriss 1st Dam

The station Ech6 marks the highest value 520 µS/cm, but also records the low value of conductivity 113µS/cm. The significant variation in conductivity between years at the station Ech6 related on the one hand to discharges loaded with high concentrations of pollutants, on the other hand to erosion and transport of fine particles to the river which can give rise to an increase in conductivity at the level of sediment. Bearing in mind the role of water evaporation which gives enrichment in ions, this increases the mineralization of sediment

The analysis of the variation of carbonate content in surface sediments of the study area (Fig. 3b) shows that these contents varied between 14.1% (Ech2) and 51.3% (Ech5) in 2018 as well as between 21.4% (Ech2) and 77.8% (Ech3) in 2019. The spatio-temporal variation (Fig. 3) does not follow any specific laws; these high contents are mainly related to the detritic origin. In fact, the waters of Oued Inaouene and its tributaries cross various limestone formations. On the other hand, the origin of the calcite can also be linked to the direct precipitation of calcite from the waters, essentially due to their high alkalinity. The carbonates, characterized by their property of adsorption of the trace metal elements (TMEs), can contribute to the increase of the contents of the latter in the sediments. The relatively high carbonate content found in most of the sediments collected at the various stations increases the risk of accumulation of TMEs in the sediments.

The loss on ignition allows identifying the rate of total organic matter in the sediments, it is among the main pollutants of the aquatic environments, and Figure 4a gives the distribution of the contents of organic matter (O.M) in the surface sediments taken in the study area. The concentrations recorded in 2019 are slightly higher than those of 2018, except for station Ech6. The concentrations vary between a maximum recorded at Ech2 in 2019 reached 2.32% and a minimum of 0.77% on Ech4 in 2018 (Fig. 4a). These levels are related to domestic, industrial (oil mill) and agricultural discharge; they can present a danger that threatens the quality of water and sediments. Generally, in dry season the organic matter present in the sediments is found with very high values explained by the fact that this season is favorable to the development of phytoplankton in the rivers and thus to the maximum productivity of the organic matter. However, the contents of organic matter that exists in all the samples remain generally weak; this can be explained by the fact that the samplings were carried out on the surface of the sediments, the organic matter undergoes an important oxidation; thereafter, it is degraded and the release of the TMEs associated with it.

The granulometry allowed determining the distribution of sediment grains along Oued Inaouene, Idriss 1st dam in categories classified according to the size of the particles and also to determine the relative proportions of these categories, in percentage of the total mass of the sediment. The analysis of the results (Fig. 5) shows a variation of the proportions of the various granulometric classes, the coarse deposits are the most dominant at the level of Inaouene (Ech4, Ech5, Ech6), and approaching the dam (Ech2, Ech3) the fine elements appear and then they dominate with a proportion that reaches 83.43%. Indeed, during

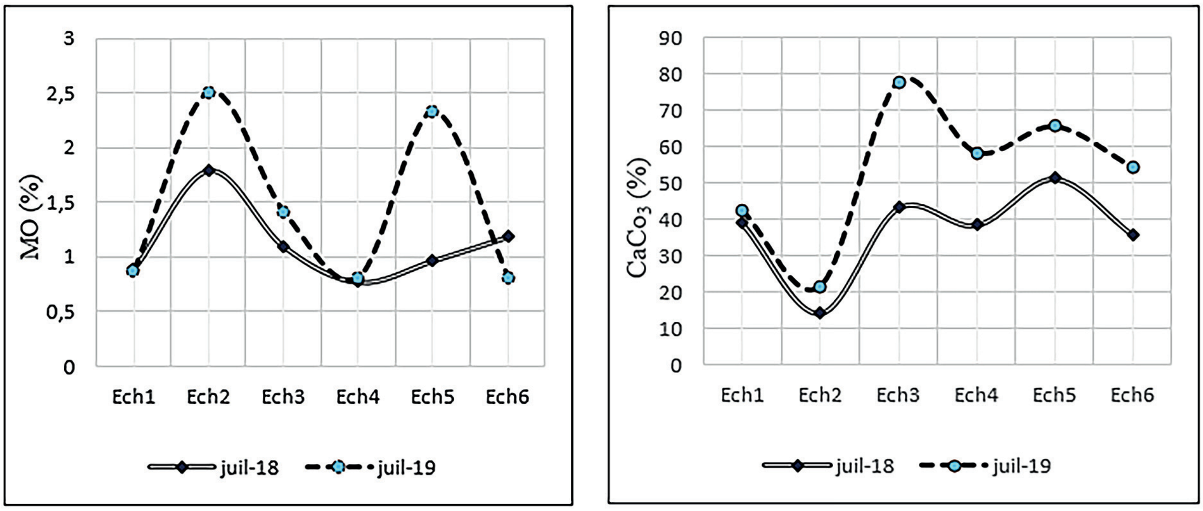


Figure 4. a) Spatial variation of loss on ignition, b) $CaCO_3$, in the sediments of Oued Inaouene, Idriss 1st dam

the rainy season, the flow tends to increase; this leads to the removal of coarser particles, which explains the abundance of sand at the level of surface sediments, while during the dry season, the flow is extremely low, and only fine particles are transported downstream which is confirmed by the results of the stations Ech2, Ech3, which is downstream of the basin and precisely at the level of the dam. On the other hand, at the level of the station E1 which is just after the dam, the gravels have a higher percentage 65.18%, so a similar character as that of the Oued Inaouene.

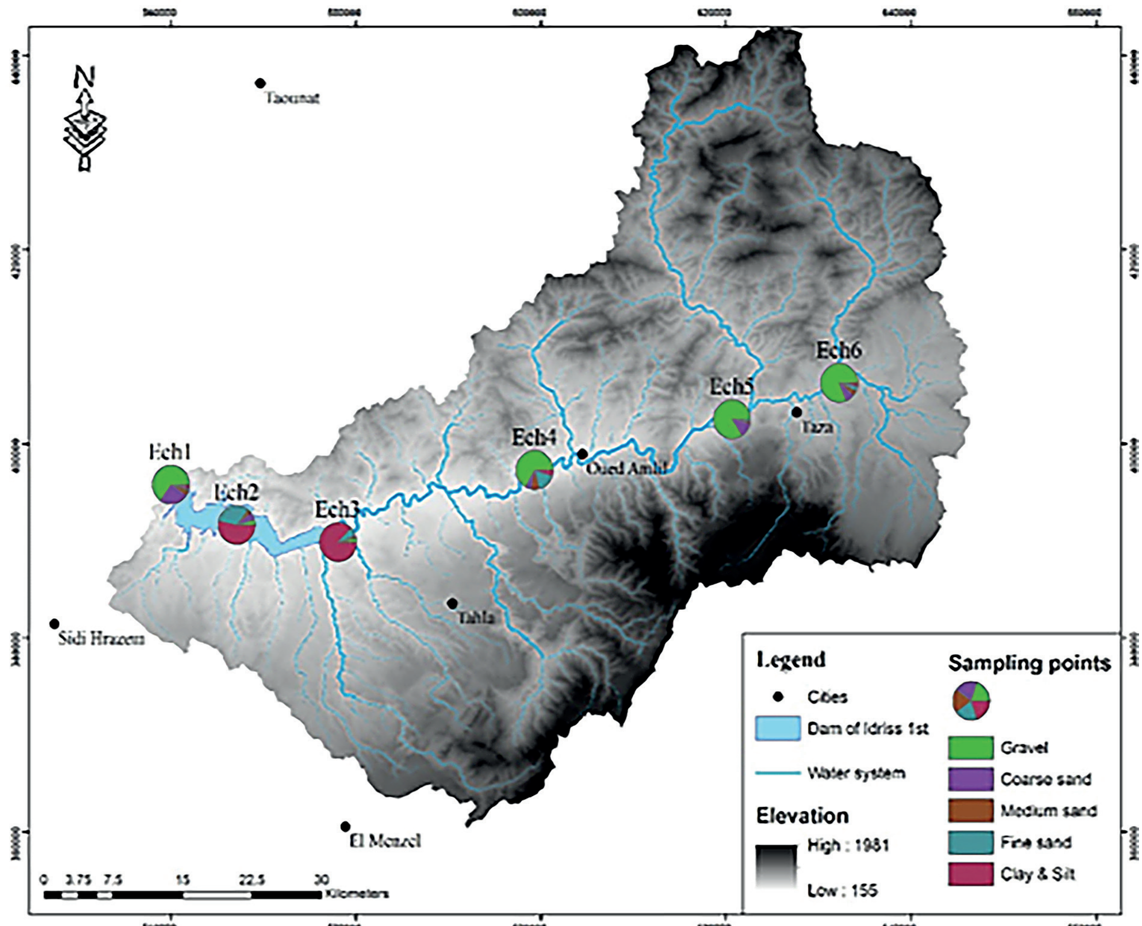


Figure 5. Distribution of particle size fractions (%) in the Oued Inaouene, Idriss 1st dam

Trace metal elements

The results of analysis of TMEs in the sediments of the Oued Inaouene (Fig. 6, 7) show a significant variability of the station Ech6 upstream of the basin to the Idriss 1st dam, some elements (Zn, P, Cu, Ba) are present with high concentrations compared to others; their evolution over the two years is almost the same, except for fluctuations at the site Ech1 and Ech6, which correspond to the sampling campaign of 2019.

Zinc

The evolution of zinc levels (Fig. 6a), is almost the same for both sampling campaigns, except a slight increase at site Ech6 during the campaign of 2018 and which records the maximum concentration 120 ppm, this can be explained by the impact of household waste discharged near this point, studies on household waste in many countries have revealed concentrations of the order of 2600 mg/kg of Zinc (Fouad, 2013). This Zn richness may also be due to well-recognized soil contamination in Morocco (Nahli et al. 2016) and often linked to various agricultural origins. Moving away from the urban area, the zinc content decreases, which explains the low impact of the natural input, the natural concentration of zinc in the earth's crust varies between 10 and 300 ppm (Tiwari et al., 2015), which allowed stating that this element is not dangerous.

Strontium

The analytical result of strontium (Fig. 6b) shows a high rate in all sites except sites (Ech6, Ech2) during the year 2018. This high rate, which reaches 915 ppm in site Ech6 for the 2019 campaign, can be explained by the impact of pollution by effluents, public dumps installed in the vicinity of Oued Inaouene. The existence of strontium related to industrial wastes, such as cathode ray tubes, dyes and varnishes etc, start to decrease when approaching the dam and its contents reach 477 ppm in site Ech2. This can be explained by a remobilization of this element from the sediments to the waters after deposition or by a dilution before sedimentation, and just after the dam the strontium increases again. On the other hand, for the campaign of 2018, the highest content reached 579 ppm at site Ech3, which is explained by a strong contribution of strontium by the sources of pollution that correspond to the discharges of the city of Oued Amlil, after a remarkable decrease was noted under the effect of dilution before the sedimentation.

Phosphorus

Phosphorus in sediments is essentially due to the contribution of particulate organic matter in the form of detritus (Alzieu, 1999). In fact, phosphorus is considered to be the factor that is at the root of the eutrophication phenomenon.

The results of phosphorus analysis in surface sediments in the sampled sites (Fig. 7b) show an almost similar evolution for the two sampling campaigns (2018, 2019). The phosphorus content varies between a maximum of 750 ppm on Ech5 in 2018 and a minimum of 291 ppm recorded on site Ech2 in 2018, but generally the concentration of phosphorus remains high on all at the level of the sites near the cities Taza and Oued Amlil, following their discharges; on the other hand, it can be natural or combined with other fertilizing elements added to increase soil fertility and transported to the river.

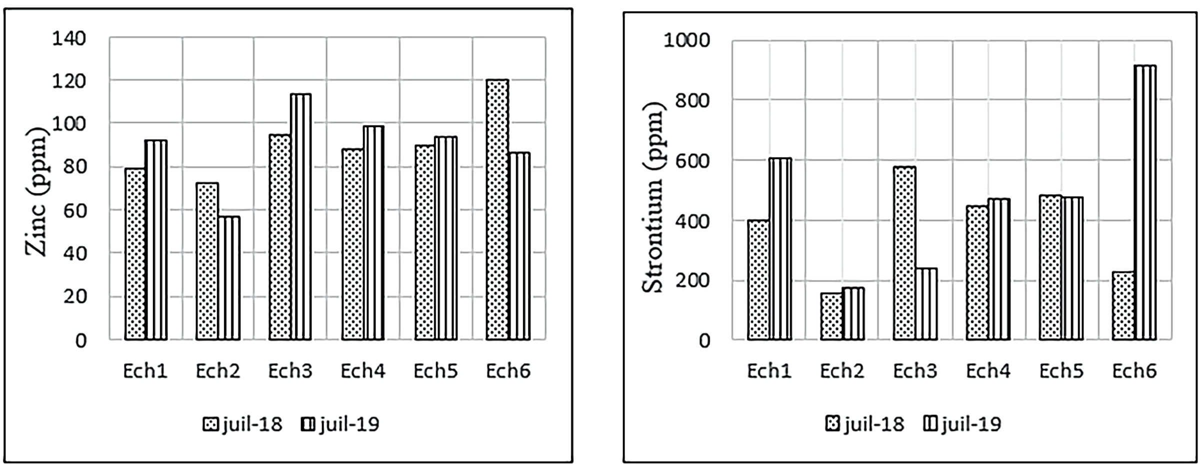
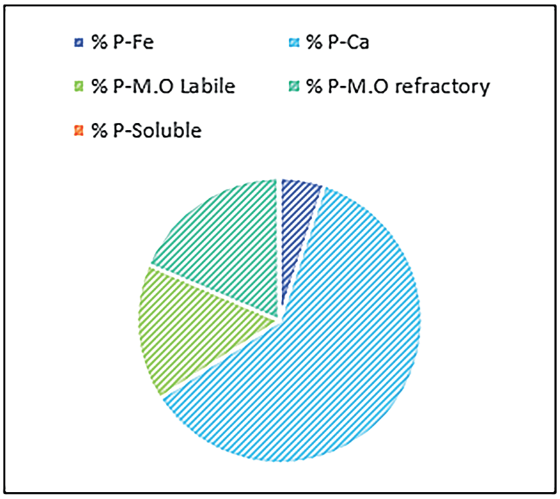


Figure 6. Variations of Zn (a) and Sr (b) contents in the studied sediments



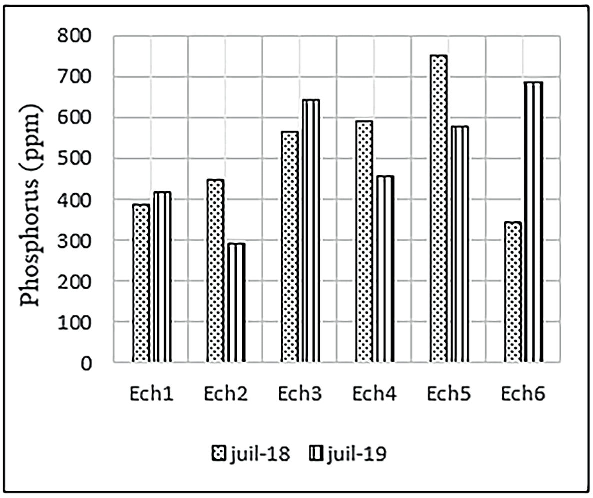


Figure 7. Phosphorus fractionation in the studied sediments (a) variations of P contents in the studied sediments (b)

Concerning the fraction of phosphorus (Fig. 7a) it can be noticed that it is found in different forms but it is essentially bound to calcium with a percentage that exceeds 50%, which is great affinity to associate with this element. The phosphorus bound to organic matter also occupies an important percentage arrives at 34%; on the other hand, the phosphorus bound to iron present with a low proportion of 5%, while the soluble phosphorus is almost negligible 0.9%.

Barium

The results of barium (Fig. 8) show the highest concentrations in the sediments of all the other elements studied, a high concentration is noted upstream Ech6 over the two years, then this concentration begins to decrease under the effect of dissolution by water, until it arrives at the minimum content that is recorded level of the dam. Then, it was noted that downstream of the basin that corresponds to the station Ech1 which is situated just after the dam, a strong increase in the contents of barium occurs. It records a maximum concentration at 1081 ppm in 2018 and 5409 ppm in 2019 ppm. This increase is of natural origin, connected to the marly substratum, rich in carbonate of barium.

Other metals

For the other metals, which present low contents compared to P, Br, Cu, Zn, the following elements were found:

Pb is a toxic metal generally present in small quantities. Indeed, the levels found in the sediments of Oued Inaouene (Fig. 9a) show a maximum value that is about 70 ppm recorded in the

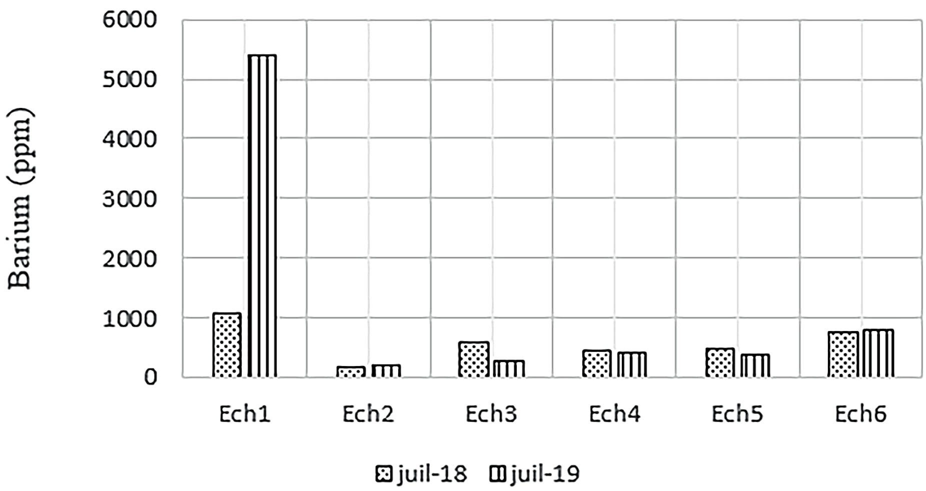


Figure 8. Variations of the Br contents in the studied sediments

station Ech5 in 2018. While in Ech6, the content recorded does not exceed 25 ppm in the same year, this campaign is characterized by the highest levels in all sites, because they are exposed to the pollution by urban effluents (Ech5, Ech4, Ech3) or agricultural discharges, in addition to a natural flow (Ech1, Ech6). Then, the results of the campaign of 2019, are characterized by lower levels compared to those of the campaign of 2018 but they exceed the guide values proposed by USEPA (EL Morhit, 2009) of the order of 40 ppm, which allowed stating that most of the sites present a medium and sometimes strong pollution.

According to the analytical results (Fig. 9b), cobalt has almost a stable value during the two years on all the sampling points except for the station Ech6, which records a high level, arrives at 28 ppm in 2018, which is probably due to pollution or else a natural source.

Cu is an essential element for all living organisms, but it is toxic at high levels. The levels of copper (Fig. 10a) found in the stations show a maximum value that is around 46 ppm in 2018 in station Ech6. While the station Ech2 at the level of the dam shows the minimum content, it does not exceed 12ppm, which means that the inputs of Cu to the dam are made but they are still less important. In fact, all the stations present the contents not exceeding 25 ppm, which remain lower than the guide values. These weak contents can be explained by the competition between the various metals, as shown by the work of Serpaud et al. (1994). The adsorption of copper is much lower than that of lead; this explains the weak contents of copper in the sediments except for site Ech6 which is considered moderately polluted, where Cu arrives via surface runoff and chemicals from these sources could potentially accumulate in the sediment.

Figure (10b) shows the variations of Ni contents in the sediments of the studied stations. The natural origin of Ni is iron oxides or iron-rich

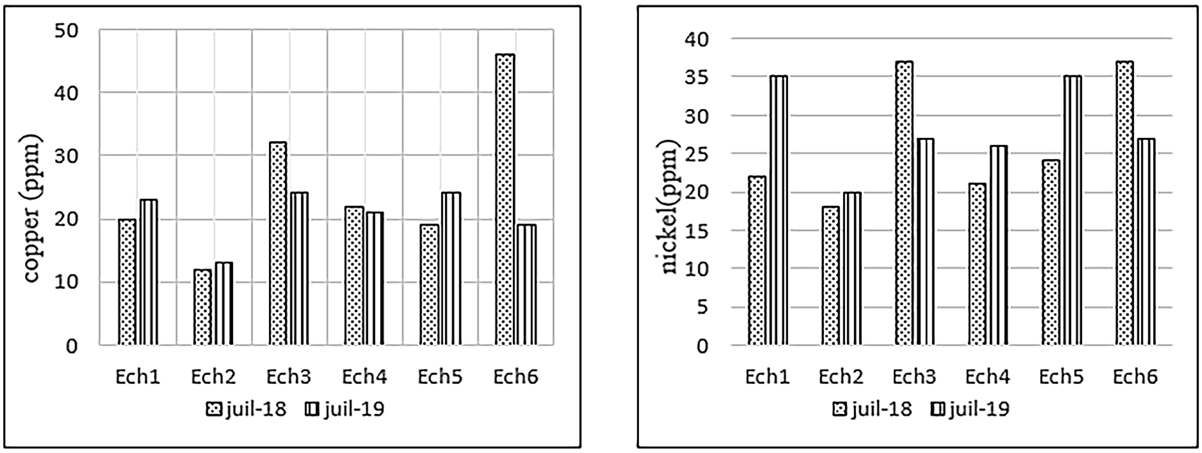


Figure 9. Variations of Pb (a) and Co (b) contents in the studied sediments

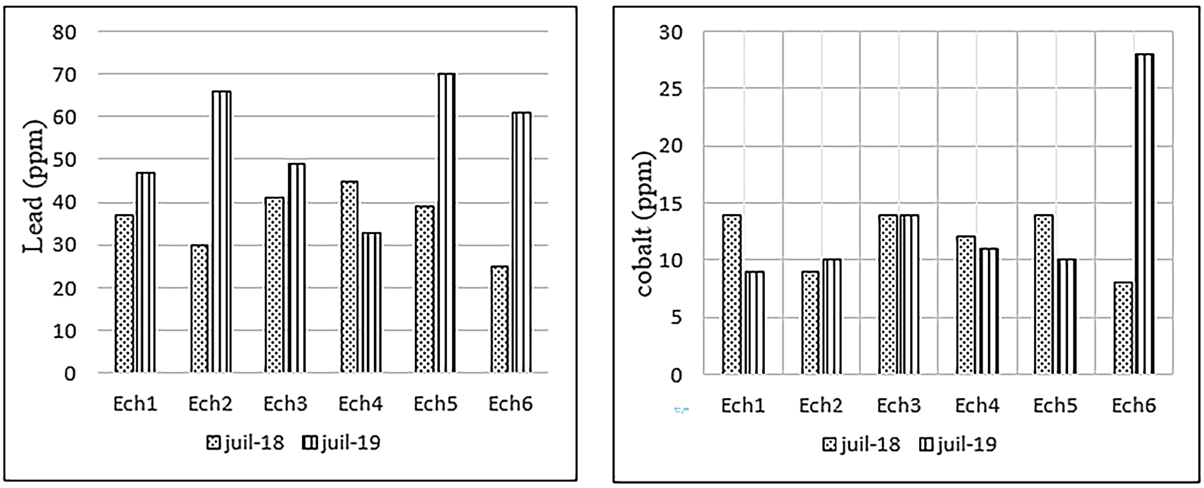


Figure 10. Variations of Cu (a) and Ni (b) contents in the studied sediments

laterites, which explains its high concentration in all the sites located in carbonate soils of the Liassic with outcrops of red clays of the Triassic, except for Ech5, which has a low value compared to the other stations.

The rest of the trace elements (Cr, Li, Ce, Zr, Y, Nb) are present with low concentrations that have no negative effect on the quality of the sediment. On the other hand, the dangerous heavy metals analyzed were below the detection limit.

Contamination index

According to Belamie and Phelippot (1982), evaluation of sediment contamination is done by comparison with the content of reference station, by calculating the contamination index:

$$Ic = \text{Measured metal content} / \text{Reference content} \quad (1)$$

In the present study, station Ech2 was chosen as the reference site given its location far from any anthropogenic disturbance and its low metal content compared to that measured at the other stations, the contamination index can be either:

- Ic > 1: an Ic > 1 indicates the beginning of contamination, its increase is accompanied by an amplification of the intensity of the contamination;
- Ic close to 1: station with little or no contamination;
- Ic < 1: essentially linked to an analytical or sampling error, or indicating the effect of significant dilution.

The average contamination index (Icm) will then make it possible to compare and characterize the stations among themselves with respect to overall pollution, in order to establish a classification according to the extent of the contamination in the entire study area:

The results of contamination index calculation show that all the stations have the contamination indices higher than 1 for all the MTE, except for Pb and P in stations Ech6 and Ech1 (Table 1) which are located upstream and downstream of the basin; they are protected and do not receive sufficient phosphorus and lead input.

The results of the contamination index calculation also show an accentuated polymetallic contamination for barium in stations Ech6, Ech1, and Ech3. This is due to the barium-bound limestone and dolomitic formations of the northern Middle Atlas and the Prerif, while the stations located at the level of the dam present the lowest contamination indices except for phosphorus in 2019, as shown by the recorded contamination indices (Table 2).

By comparing the classification of the stations according to their average contamination index, the following decreasing order of contamination is obtained:

- In 2018: Ech6 > Ech1 > Ech5 > Ech4 > Ech2
- In 2019: Ech1 > Ech6 > Ech5 > Ech4 > Ech2

This further confirms the negative impact of geological discharges entering the river system by erosion.

Table 1. Spatial variations in contamination indices (CI) in 2018

Stations	Ic P	Ic Zn	Ic Co	Ic Cu	Ic Ni	Ic PB	Ic Ba	Ic Sr	Σ Icm
Ech1	0.9	1.1	0.9	1.7	1.2	0.7	6.0	2.6	1.9
Ech2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ech3	1.3	1.3	1.4	2.7	2.1	0.7	3.2	3.7	2.0
Ech4	1.3	1.2	1.1	1.8	1.2	0.5	2.4	2.8	1.5
Ech5	1.7	1.3	1.0	1.6	1.3	1.1	2.7	3.1	1.7
Ech6	0.8	1.7	2.8	3.8	2.1	0.9	4.2	1.5	2.2

Table 2. Spatial variations in contamination indices (CI) in 2019

Stations	Ic P	Ic Zn	Ic Co	Ic Cu	Ic Ni	Ic PB	Ic Ba	Ic Sr	Σ Icm
Ech1	1.4	1.6	1.6	1.8	1.8	1.2	27.5	3.5	5.0
Ech2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ech3	2.2	2.0	1.6	1.8	1.4	1.4	1.4	1.4	1.6
Ech4	1.6	1.7	1.3	1.6	1.3	1.5	2.1	2.7	1.7
Ech5	2.0	1.6	1.6	1.8	1.8	1.3	1.9	2.7	1.8
Ech6	2.4	1.5	0.9	1.5	1.4	0.8	4.1	5.2	2.2

Principal component analysis

Relationship between metals

The correlation plots above, obtained by XLSTAT software, were used to determine the relationships that may exist between the metals studied (Table 3 and 4). According to Waris et al. (2010), the correlation coefficient determines the relationship between two variables and measures the strength of that relationship. Positive correlations and trends suggest a partly common origin and/or chemical similarities. This common origin may be natural and/or related to anthropogenic activity. Negative trends may be the consequence of different chemical behavior between metals.

The analysis of the correlation matrix tables revealed a good correlation between lead, copper, cobalt, zinc, and nickel; on the other hand, strontium does not present a link with any of these metals except nickel for the samples of 2019 (Table 4). Lead is the only trace metal element showing a fairly good correlation with carbonates, while the other metals present a good correlation with conductivity (Fig. 11). In 2018 (Table 3) the correlation is positive between the metals mentioned before, but in a weak way; in turn, most of the metals are strongly correlated with carbonates. The organic matter is inversely proportional to the pH, in fact, the oxidation of the organic matter leads to a decrease in pH. All the trace metal elements (TMEs) present a poor correlation with organic matter; therefore, the latter has little influence on the adsorption and accumulation of TMEs in the analyzed sediments.

Table 3. Correlation matrix between sediment metals and physicochemical parameters measured at sites sampled in 2018

Variables	p	Zn	Co	Cu	Ni	PB	Ba	Sr	pH	CE	$CaCO_3$ (%)	Mo (%)	Fraction <36	Fraction >36
p	1													
Zn	-0.1910	1												
Co	-0.4866	0.9260	1											
Cu	-0.3682	0.9596	0.9265	1										
Ni	-0.1801	0.8392	0.7610	0.9085	1									
PB	0.0733	0.0754	0.1687	-0.0505	0.0448	1								
Ba	-0.4255	0.2769	0.2081	0.3883	0.3039	-0.2462	1							
Sr	0.6447	0.0104	-0.3327	0.0224	0.2546	-0.4131	0.2144	1						
pH	0.4500	0.1273	0.0933	-0.0950	-0.2456	0.1364	-0.7352	-0.2199	1					
CE	0.8479	-0.2700	-0.4658	-0.3812	-0.0424	0.3971	-0.4753	0.5198	0.1852	1				
$CaCO_3$ (%)	0.5655	0.3678	0.0040	0.2845	0.3710	-0.1516	0.4405	0.8206	0.1023	0.3550	1			
Mo (%)	-0.3412	-0.2350	0.0782	-0.2028	-0.1293	0.6041	-0.5451	-0.7210	0.0950	0.0601	-0.8346	1		
Fraction <36	0.0098	-0.1940	-0.1166	-0.0387	0.2953	0.0365	-0.3816	0.1684	0.2709	0.4002	-0.2938	0.4903	1	
Fraction >36	-0.0098	0.1940	0.1166	0.0387	-0.2953	-0.0365	0.3816	-0.1684	0.2709	-0.4002	0.2938	-0.4903	-1.0000	1

Table 4. Correlation matrix between sediment metals and physicochemical parameters measured at sites sampled in 2019

Variables	p	Zn	Co	Cu	Ni	Pb	Ba	Sr	pH	CE	$CaCO_3$ (%)	Mo (%)	Fraction <36	Fraction >36
p	1													
Zn	0.6544	1												
Co	0.0808	0.6845	1											
Cu	0.5713	0.9041	0.8310	1										
Ni	0.3152	0.4897	0.6921	0.8070	1									
PB	-0.0652	0.6551	0.7997	0.6171	0.2980	1								
Ba	-0.2434	0.0538	0.3435	0.2782	0.5809	0.0045	1							
Sr	0.4993	0.1086	-0.2902	0.1952	0.4066	-0.4165	0.3299	1						
pH	0.1454	-0.3630	-0.5839	-0.2725	0.0182	-0.4439	-0.2018	0.6752	1					
CE	0.6909	0.0560	-0.4914	0.0450	0.1180	-0.5044	-0.2281	0.8336	0.7864	1				
$CaCO_3$ (%)	0.4200	-0.1507	-0.7850	-0.3230	-0.3247	-0.5878	-0.2642	0.7091	0.7152	0.8515	1			
Mo (%)	-0.3473	-0.4990	-0.0066	-0.3519	-0.1942	-0.1108	-0.4250	-0.6375	0.0892	-0.3357	-0.4676	1		
Fraction <36	-0.0136	0.0864	0.0695	-0.1491	-0.5205	0.0709	-0.3538	-0.7350	0.7718	-0.5112	-0.3392	0.3303	1	
Fraction >36	0.0136	-0.0864	-0.0695	0.1491	0.5205	-0.0709	0.3538	0.7350	0.7718	0.5112	0.3392	-0.3303	-1.0000	1

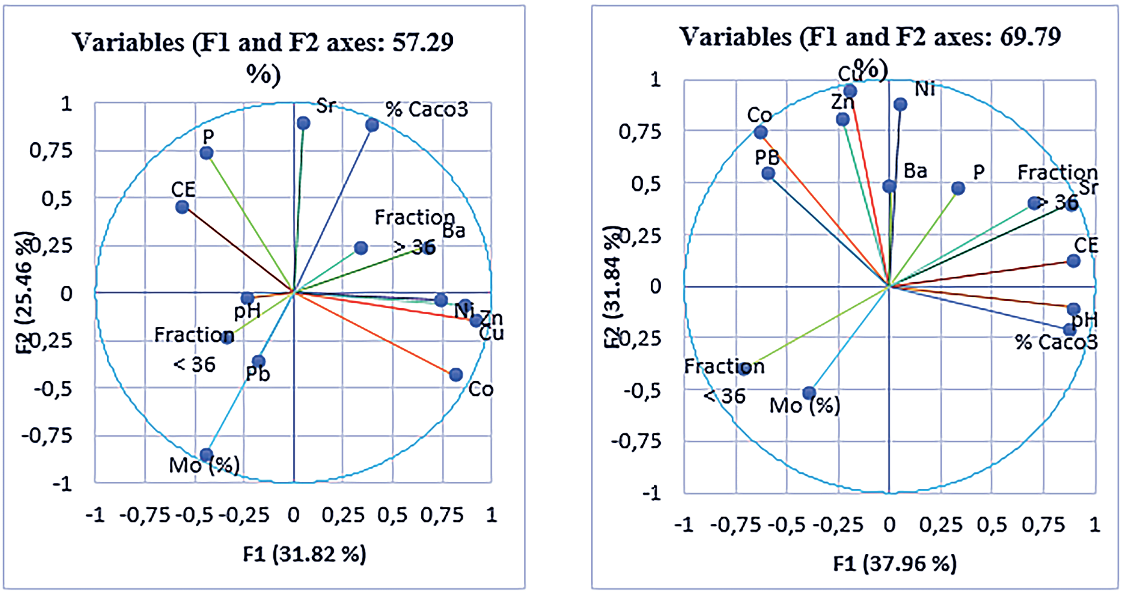
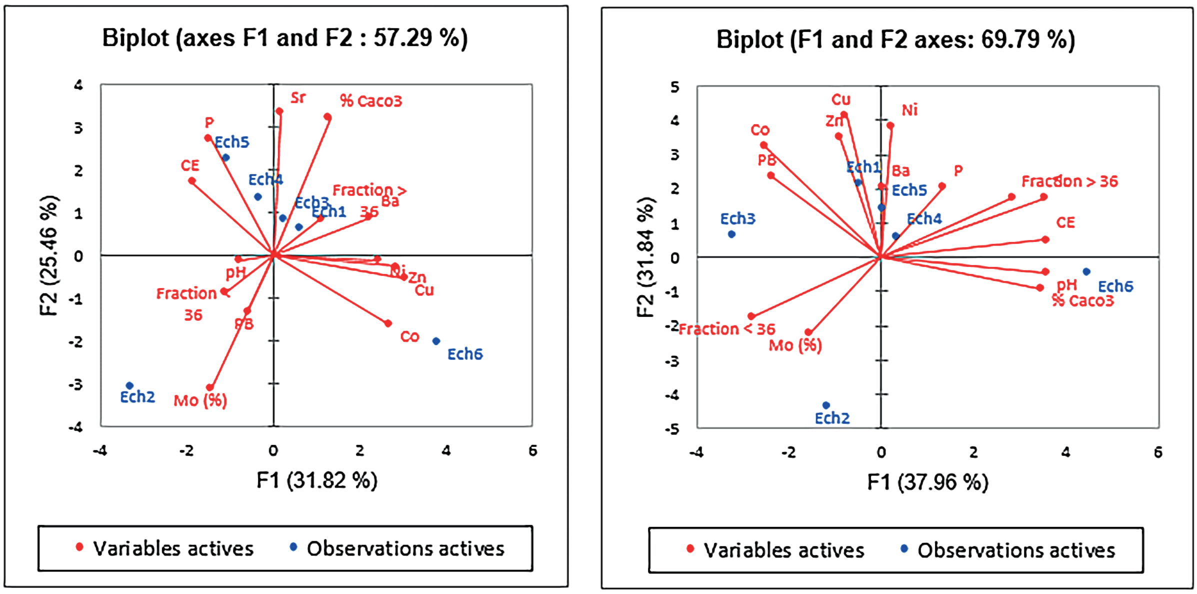


Figure 11. The correlation circle for trace metal elements at sites sampled in 2018 (a) and 2019 (b)

Axis meanings and data analysis

The projection of variables and individuals was performed on 2 axes, which represent 57.92% of the total variance. Axis 1 accounts for 31.82% of the total variance, and the second axis for 25.46% (Fig. 11a). The PCA results show a strong positive correlation between the following: (Ni; Zn), (Zn; Co), (Cu; Zn), (Cu; Ni), and Ba with fraction > 36 and they are related to the main component F1, the high correlation coefficient between the different metals mean that they arrived from the same source or source rock that influences the concentrations of heavy metals (Huang Xa et al., 2010). On the other hand, Sr, Mo, Pb and P are related to the second component F2 which expresses the influence of organic matter on these metal elements.

Examination of the correlation circle obtained among the PCA results of the 2019 campaign (Fig. 11b) shows that the first two axes determine 69.79% of the total information (37.96% for axis 1 and 31.84% for axis 2). In addition to strontium, the physico-chemical parameters ($CaCo_3$, pH, EC) are strongly related to F1; in



Sites sampled in 2018

Sites sampled in 2019

Figure 12. Representation map of individuals (sampled sites) based on factorial axes

turn, most of the TMEs are related to the F2 axis. These results mean that the afore-mentioned elements have common, reciprocal sources and an identical conduct during transport. For Co, P, and Pb, it will be preferable to interpret them on the F2/F3 axes.

The graph above corresponds to one of the objectives of PCA. It allows representing the individuals on a two-dimensional map, and thus identifying trends.

The projection of the individuals on the F1–F2 factorial plane shows the individualization of 4 main groups (Fig. 12):

- Group 1: located on the positive side of the F1 axis and constituted by stations Ech5 and Ech4 for the sites sampled in 2019, it is characterized by high levels of ETM (P, Ba, Ni), as well as high pH and the fraction higher than 36. In 2018, it is constituted by Ech3 and Ech1, which are characterized by the presence of significant levels of strontium and carbonate;
- Group 2: located on the negative side of the F1 axis and formed by station Ech2 on both years, it is characterized by low levels of TMEs and low electrical conductivity; however, these stations have high levels of organic matter, and fraction below 36;
- Group 3: located on the negative side of the F1 axis, is constituted by stations Ech4 and Ech5 in 2018 and which is characterized by important contents of phosphorus but it is poor in ETMs; on the other hand, in 2019 stations Ech4 and Ech5 – compared to the other groups – have a mixture between physical parameters and TMEs;
- Group 4: represented by station Ech6, characterized by the maximum of TMEs in 2018 (Co, Cu, Ni, Zn) these present very good correlations with the F1 axis. This station in 2019 has a very high pH and carbonate content.

CONCLUSIONS

The analyses carried out concerned the surface sediments integrating the recent contributions. They allowed characterizing the sediments from a particle point of view in majority coarse granulometry at the level of Oued Inaouene and at the arrival at the dam the fine elements become the most dominant; the sediments present a very high percentage of carbonate, but low from the point of view of organic matter.

The analysis of the trace metal elements has highlighted an important contamination of natural origin and approximately of urban agglomerations (Taza, Oued Amlil) that generate large quantities of wastewater without any prior treatment and solid waste that are discharged directly to Oued Inaouene. In fact, the spatial variation of TMEs shows that an increase in the Ba, Sr, P, Cu, and Pb contents is favored by the physicochemical conditions of the environment. Indeed, the alkaline pH of the water favors the precipitation of TMEs and limits their liberation in the water, and this induces an intense enrichment in TMEs of the sediments. The analysis of sediments shows the absence of heavy metals dangerous for public health (Ag, Cd, Hg), which were below the detection limit, despite the diversity of sources of anthropogenic pollution in the study area. This allowed concluding that the sediments of Oued Inaouene and its main tributaries do not raise any ecological concern.

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