

Statistical approach of heavy metals (Mo, Co, Cd, Ni, Sb, Bi) in the sediments of the MFOUATI river (south of Congo Brazzaville)

ABSTRACT

Aims :

The general objective of this study was to evaluate heavy metals (Mo, Co, Cd, Ni, Sb, Bi) in the sediments of the Mfouati River near the area impacted by the mining operation.

Study Design:

The sediments were collected in the area near the abandoned plant and in the vicinity. At the end of the sampling, the samples were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Place and Duration of Study:

Sediments were collected in the Mfouati River near the area impacted by the mining operation, these samples were taken in September 2021.

Methodology : X-ray diffraction was performed on the sediments of the Mfouati River, the physico-chemical parameters were measured with a Hanna type apparatus. The contents of heavy metals (Mo, Co, Cd, Ni, Sb, Bi) in the sediments were measured by optical emission spectroscopy (ICP-OES). The level of metallic contamination, the indices of evaluation of the contamination (FC, FE, Igeo) were calculated by using the expressions which exist in the literature.

Results : The results obtained show that the physical-chemical parameters (pH, EC and TDS) measured are within the standards (WHO). Only the pH which presents a slightly acid character at the stations (S4, S5, S6). The heavy metal contents found (mg/Kg) vary between Mo: [0,05-23] ; Co:[10-39] ; Cd[0,1-63] ; Ni[7-36] ; Bi[0,164-0,169] ; Sb[1-29]. X-ray diffraction showed the presence of the following minerals: Talc and Kaolinite. The results of contamination factor showed the following order:FC(Cd)> FC(Sb) >FC(Mo) >FC(Co) >FC(Bi) >FC(Ni);enrichment factor the order is as follows: FE(Cd)>FE(Sb)>FE(Fe) >FE(Bi) >FE(Mo); geo accumulation index the order is as follows:Igeo(Ni)>Igeo(Co) >Igeo(Mo) >Igeo(Sb) >Igeo(Cd) >Igeo(Bi).

Conclusion : The levels of metals Co, Cd, Ni, Sb, Mo in the sediments of the Mfouati River are higher than the concentrations in the terrestrial crust.

Keywords: Sediments, heavy metals, contamination factor, factorial analysis

1. Introduction

Every day in the world hundreds of tons of pollutants (polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), pesticides and heavy metals are discharged into the environment. These heavy metals are considered serious pollutants of the aquatic environment, because of their persistence and tendency to bioaccumulate in sediments [1-2]. They enter the aquatic environment through atmospheric deposition, water runoff, and direct discharge [3]. Once they arrive in this environment, they partition between the different compartments (water and sediment) [4-5]. Metals bound to sediments are likely to be released into the water column; during changes in environmental conditions such as redox potential, pH, desorption [6]. Indeed the accumulation of toxic metals will lead to high concentrations and beyond a certain threshold they become dangerous for the environment and for human health [7]. The Mfouati River located in the Bouenza Department (southern Congo Brazzaville) is a tributary of the Niari River. This river has been influenced by mining activities from the activities of the poly-metal ore processing plant. This plant is currently in total abandonment. The Mfouati River is located in front of the abandoned plant and receives heavy metals from water runoff. It is in this perspective that we propose to evaluate the heavy metal content in the sediments of the Mfouati River.

2. MATERIALS AND METHODS

2.1. Study area

Mfouati is a locality located in southwestern Congo, in the Bouenza department, at an average altitude of 441 meters. It is the chief town of the Mfouati district and its geographic coordinates are: 4°23'26"S and 13°48'41"E. The Mfouati district has an area of 560 km², bordered to the east by the Mindouli district in the Pool department, to the west by the Boko-songho district, to the north by the Yamba and Bouansa districts, and to the south by the Central Congo DRC. The department of Bouenza is one of the departments of Congo marked by an important agricultural activity.

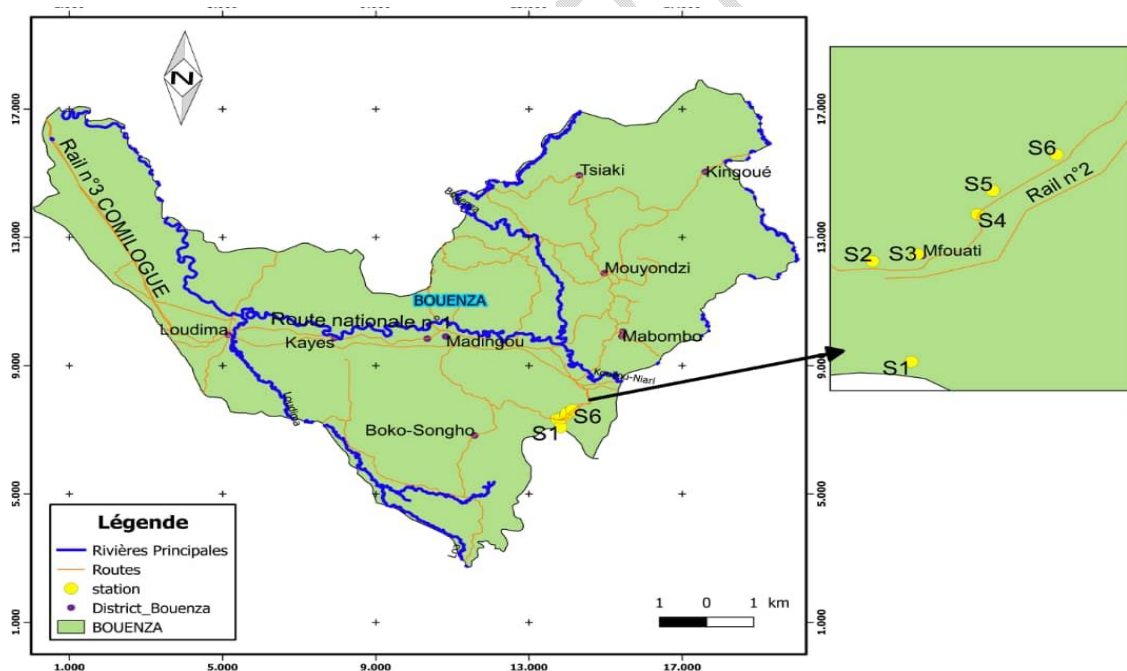


Figure 1: Mfouati study area

2.2. Sediment Sampling

A sampling campaign was conducted in September 2021 during which six stations were selected. At each station, surface sediments were collected at a depth of 10 to 20 cm. Sampling was done with a plastic hand scoop until a representative mass of approximately 1 kilogram was obtained. The wet

samples collected for each station were placed in food grade plastic bags, labeled and transported to the laboratory.

2.3. Preparation and analysis

The samples arrived at the laboratory, were dried in ambient air. After drying, each sample was stirred properly until a homogeneous mixture representative of the station considered was obtained. A 2 mm sieve was used to remove plant debris and coarse particles. Then the sediments were crushed and sieved with a 90 µm sieve. The particle size analysis was performed using the Robinson pipette method based on Stokes. The Walkley and Black method was applied to determine the organic matter content [8]. The pollution level of each metal in the sediment samples was determined using the contamination factor (CF), geo-accumulation index (Igeo), pollutant loading index (PLI), potential ecological risk assessment. The characterization of minerals was performed using X-ray diffraction.

2.4. Procedure

A mass of 0.5 g of dry sample was mixed with a mixture of nitric acid (HNO₃) and hydrochloric acid (HCl), in the proportions 1:3 (1V/3V). The whole was heated in a digestion block for 30 min. After dry evaporation, the residue is diluted in 50 ml of deionized water. The sample is filtered through a membrane and analyzed by optical emission spectroscopy (ICP -OES).

Table 1: Relative contents of the continental crust according [9].

Métaux	Mo	Co	Cd	Fe	Ni	Sb	Bi
UCC	1,4	12	0,102		19	0,123	0,31

2.6. Assessment of metal contamination in Mfouati River sediments

To assess metal pollution, we used the pollution indices.

2.6.1. Contamination factor (CF)

The contamination factor or CF is one of the factors used to evaluate the contamination of a metal analyzed in a sediment. It is expressed as the ratio between the content of the metal in the sediment (Cs) and the content of the same metal in the geochemical background of the watershed of the study area concerned (Cb) [10-11].

$$FC = \frac{\text{Concentration of metal in sediment}}{\text{Background concentration of metal in crust}}$$

Table 2: Contamination factor class

Facteur de contamination (FC)	class	Category
CF is less than 3	class1	uncontaminated
CF is between 3 and 10	class 2	Polluted
CF is greater than 10	class 3	A great risk

2.6.2. Enrichment Factor

The enrichment factor (EF) is commonly used as a first approach in metal source approach in the determination of metal sources [15-17]. In our study, the metal enrichment factor of the studied sediments was calculated by normalizing to Iron according to the following formula:

$$FE = \frac{\frac{(\text{Metal content})_{\text{sediment}}}{(\text{Fe content})_{\text{sediment}}}}{\frac{(\text{Metal content})_{\text{reference}}}{(\text{Fe content})_{\text{reference}}}}$$

with :

CF: contamination factor; n: number of metals.

PLI > 1 : presence of pollution ; PLI < 1 : no pollution

Table 3: Classification of enrichment factor values

Class	Valeur	Pollution intensity
1	$FE \leq 2$	Low Enrichment
2	$2 < FE < 5$	Moderate Enrichment
3	$5 < FE < 20$	Significant enrichment
4	$20 < FE < 40$	Very strong enrichment
5	$FE > 40$	Extreme Enrichment

2.6.3. Geo-accumulation index

The index was introduced by Muller in order to determine the degree of metallic contamination in sediments [18]. It is calculated according to the following equation:

$$I_{geo} = \log_2 (C_n / 1.5 B_n)$$

With : I_{geo} geo accumulation index

C_n : Concentration in the sediment for element n

B_n : Geochemical background for element n.

1,5 : correction factor taking into account the natural fluctuations of the content of a given substance in an environment and the weak anthropic influences. The following table shows the class of geo-accumulation indices.

Table 4: Geo-accumulation index classification

Class	Value	Pollution intensity
0	$I_{geo} < 0$	Not polluted
1	$0 < I_{geo} < 1$	Not polluted to moderately polluted
2	$1 < I_{geo} < 2$	Moderately polluted
3	$2 < I_{geo} < 3$	Moderately to severely polluted
4	$3 < I_{geo} < 4$	Severely polluted
5	$4 < I_{geo} < 5$	Severely to very severely polluted
6	$5 < I_{geo}$	Very severely polluted

2.6.4. Ecological Potential Risk Assessment

The ecological potential risk index was established by Hakanson [19]. It is used to calculate the high level of toxicity of different metal ions. The ecological risk assessment of heavy metals in sediment samples is given by the ecological risk (Er) and the risk index (RI).

$$Er^i = Tr \cdot Cf^i$$

Er^i : potential ecological risk factor

Tr = toxic response factor, Cf^i : contamination factor

The toxic response factor (Tr) of the following metals Mo, Co, Cd, Ni, Sb :15, 5, 30, 5, 40.

3. Results and discussion

3.1. Mineralogical analysis of Mfouati River sediments

The diffractograms of the six samples of sediments collected in the Mfouati River, reveal the presence of characteristic peaks. The observation of these diffractograms shows us the presence of two clay species, namely Talc and Kaolinite. These clay species are associated with impurities of Quartz and Iron. The peaks corresponding to $2\theta = 9; 73$ reflect the presence of talc in the sediment. The intensities of these peaks being low, this tells us about the non abandonment of these species in the sediments. The values of the peak at $2\theta = 12(20; 26; 64)$ indicate the presence of Kaolinite in the sediments of the Mfouati River. This result is in agreement with those obtained by (Moutou , 2012) who had revealed the presence of Kaolinite as the only clay species. Kaolinite is in abandonment compared to talc in the Mfouati River sediments. The peak values at $2\theta = 21(26, 42, 46, 50, 55, 76, 80)$ show the presence of quartz in the sediments. The intensities of these peaks being large indicates the abandonment of these species in these samples. The peak corresponding to $2\theta = 24(35; 60)$ indicates the presence of iron in the sediments. The line at $2\theta = 60$ of Iron, is more intense than that of Kaolinite and talc, which tells us about the abandonment of this element in the sediments. The diffractogram below shows the XRD spectra for the sediments of the six stations collected in the Mfouati River.

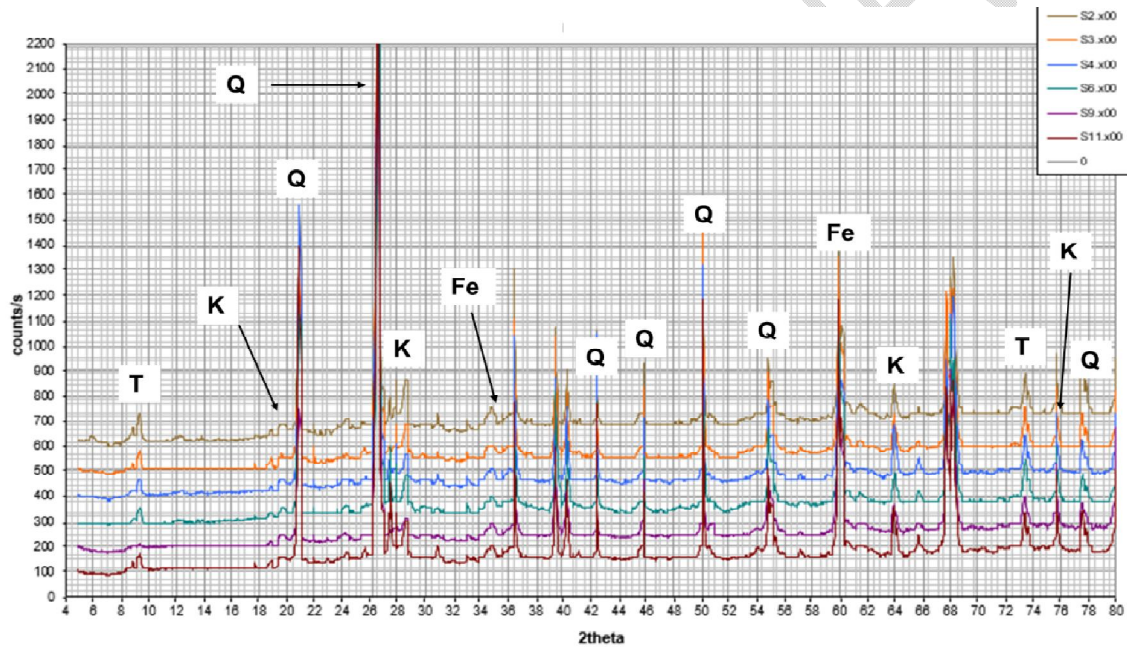


Fig. 2: diffractogram of the Loutété River sediments

3.2. Physico-chemical of the sediments Mfouati River

The results of the physico-chemical analysis of the sediments of the Mfouati River are reported in the table below:

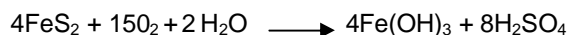
Table 5: Characteristics of the surface sediments of the Mfouati River

Station	S1	S2	S3	S4	S5	S6
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pH	6,1	6,2	5,9	5,7	4,58	5,68
CE(µs/cm)	231,7	140,1	80,86	58,2	76,7	124,6
Argile (%)	2,7	2,9	11,9	4,9	3,5	0,9
LF (%)	7,1	12,4	13,1	10	8,5	3,2
LG (%)	12,5	9,5	10,6	8,3	7,2	9,3
SG (%)	52,5	48,02	36,2	50,3	59,3	60,7
SF (%)	23,2	22,4	24,3	18,4	13,6	20,5
MO (%)	0,21	0,29	2,29	0,25	0,15	0,26

MO: organic matter, SF: fine sand, SG: coarse sand, LG: coarse silt, LF: fine silt

The pH values presented in the table show a maximum pH for S2 (6.2) and a minimum pH for S6 (4.58). This pH is slightly acidic and consistent throughout the river for stations S1, S2. Overall, the sediments have a weakly acidic nature. This acidity can be explained by the presence of sulfide minerals such as pyrite (FeS₂) [21].



The electrical conductivity varies between a maximum of 231.7µs/cm (S1) and a minimum of 58.2 µs/cm (S4). The electrical conductivity of a solution is due to the movement of ions. The conductivity values observed in the sediments are typical of those observed in freshwater sediments (EC < 750 µs/cm). The low values of electrical conductivity inform us that these ions are adsorbed in other phases. With regard to the results of the clay fraction, we can see that the sandy fraction is more dominant than the other fractions.

3.3. Concentration of heavy metals in sediments

The table below presents the concentrations of heavy metals in the sediments of the Mfouati River.

Table 6: Concentration of heavy metals in sediments

Stations	Mo	Co	Cd	Ni	Bi	Sb
S1	4	18	13	22	0,165	16
S2	23	16	63	12	0,166	29
S3	12	39	18	24	0,167	10
S4	8	37	11	36	0,168	6
S5	0,05	15	0,6	16	0,169	1
S6	7	10	0,1	7	0,164	2
Minimum	0,05	10	0,1	7	0,164	1
Maximum	23	39	63	36	0,169	29
Average	9,008	22,5	17,61	19,5	0,16	10,66
Ecart-type	7,93	12,30	23,32	10,23	0,001	10,53
UCC*	1,4	12	0,1	19	0,123	0,31

UCC : concentration of heavy metals in the earth's crust

The Molybdene content is between 0.05 and 23 mg/kg. On average, the Molybdene content is higher than that of the earth's crust, which is 1.4. The Cobalt concentration varies between 10 and 39 mg/kg. On average the Cobalt concentration is higher than that of the earth crust which is 12 mg/Kg. The Cadmium content varies between 0,1 and 63 mg/Kg. On average this concentration is higher than that of the earth's crust which is 0,1 mg/Kg. The Nickel content varies between 7 and 36 mg/Kg. On average the Nickel concentration is equal to that of the earth's crust. The concentration of Bismuth varies between 0,164 and 0,169. On average the content of Bismuth is lower than that of the earth's crust. The antimony concentration varies between 1 and 29 mg/kg. On average this concentration is

higher than that of the earth crust which is 0,31 mg/Kg. The figures below show the distribution of heavy metals in the sediments of Mfouati.

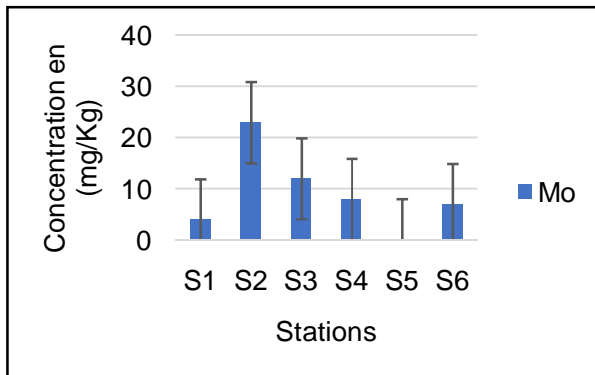


Fig. 2-a: Cobalt distribution

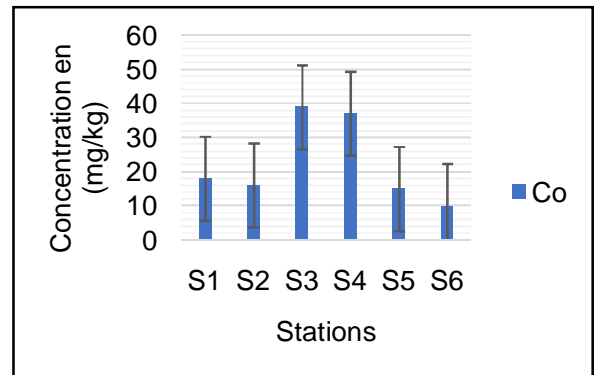


Fig. 2-b: molybdene distribution

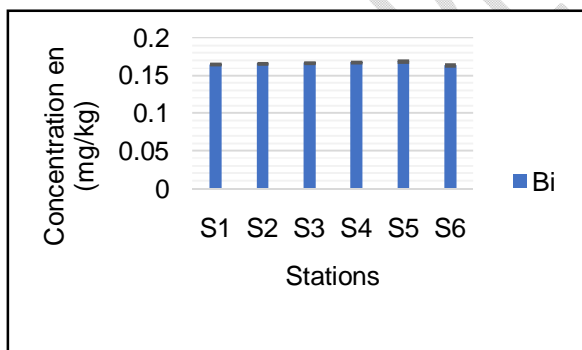


Fig. 2-c : Nickel distribution

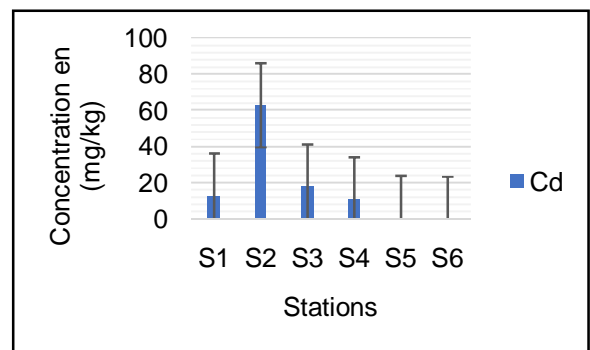


Fig. 2-d : Cadmium distribution

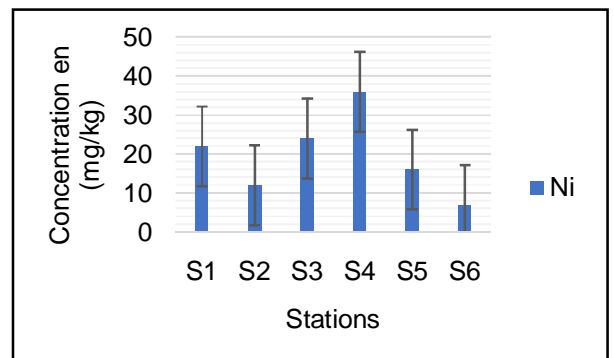
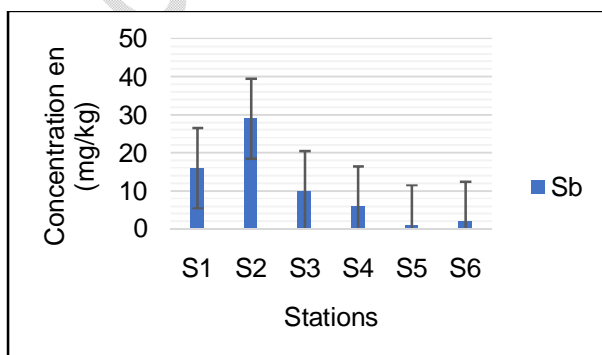


Fig. 2-e: Nickel distribution

Fig. 2-e : bismuth distribution

Fig.2-f : Antimony distribution

3.4. Assessment of metal contamination in Mfouati River sediments

The table below presents the values of the contamination factor

Table 7: Contamination factor in the sediments of Mfouati

Stations	Contamination factor					
	Mo	Co	Cd	Ni	Bi	Sb
S1	2,85	1,5	127,45	1,15	1,34	51,61
S2	16,42	1,33	617,64	0,63	1,35	93,54
S3	8,57	3,25	176,47	1,26	1,36	32,25
S4	5,71	3,083	107,84	1,89	1,37	19,35
S5	0,035	1,25	5,88	0,84	1,37	3,22
S6	5	0,833	0,98	0,36	1,33	6,45
Min	0,035	0,83	0,98	0,36	1,33	3,22
Max	16,42	3,25	617,64	1,89	1,37	93,54
Mean	6,43	1,87	172,71	1,02	1,36	34,4

Cadmium and antimony have contamination factor values greater than 10 in stations (S1, S2, S3, S4), which means that these metals present a great risk for the sediments of the Mfouati River. On the other hand, molybdenum is polluted at the stations (S2 and S3). On average the $FC(Cd) > FC(Sb) > FC(Mo) > FC(Co) > FC(Bi) > FC(Ni)$. The figure below shows box plots of metal contamination factors.

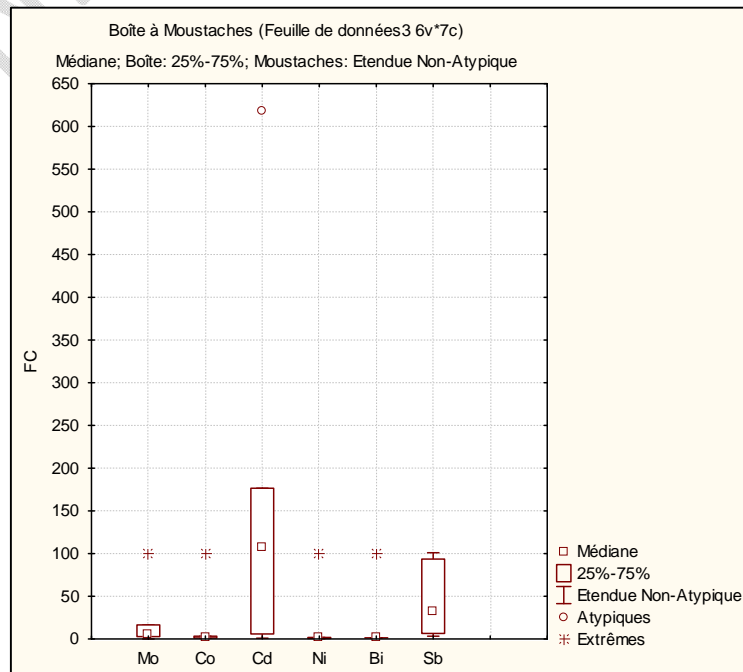


Fig. 3: Box plots of metal contamination factors

3.4.1. Geo-accumulation index

The table below shows the values geo-accumulation index

Table 8: Geo-accumulation index

Stations	Igeo					
	Mo	Co	Cd	Ni	Bi	Sb
S1	1,9	7,16	-0,17	8,12	-6,2	1,72
S2	4,42	7	2,09	7,24	-6,19	2,58
S3	3,48	8,28	0,29	8,24	-6,19	1,04
S4	2,9	8,2	-0,41	8,83	-6,18	0,31
S5	-4,42	6,9	-4,61	7,66	-6,17	-2,27
S6	2,7	6,32	-7,2	6,47	-6,21	-1,27
Min	-4,42	6,32	-7,2	6,47	-6,21	-2,27
Max	4,42	8,28	2,09	8,83	-6,17	2,58
mean	1,83	7,31	-1,67	7,76	-6,19	0,35

The mean values of Bi and Cd vary between - 6.19 and -1.67 respectively. The Bi in all the stations does not present any contamination because $I_{geo} < 0$. The Cd does not present any contamination in the stations (S1, S4, S5 and S6) except in the station S2 where the Cd presents a not polluted to moderately polluted state and in the station S3 where the Cd is in the moderately polluted to severely polluted state. Co and Ni in all stations show I_{geo} values > 5 which shows that Co and Ni are very severely polluted in the stations. Mo in stations S2 and S4 shows a severely polluted state against a moderately to severely polluted state in station S4. On average $I_{geo}(Ni) > I_{geo}(Co) > I_{geo}(Mo) > I_{geo}(Sb) > I_{geo}(Cd) > I_{geo}(Bi)$. The figure below shows box plots of the I_{geo} index for metals.

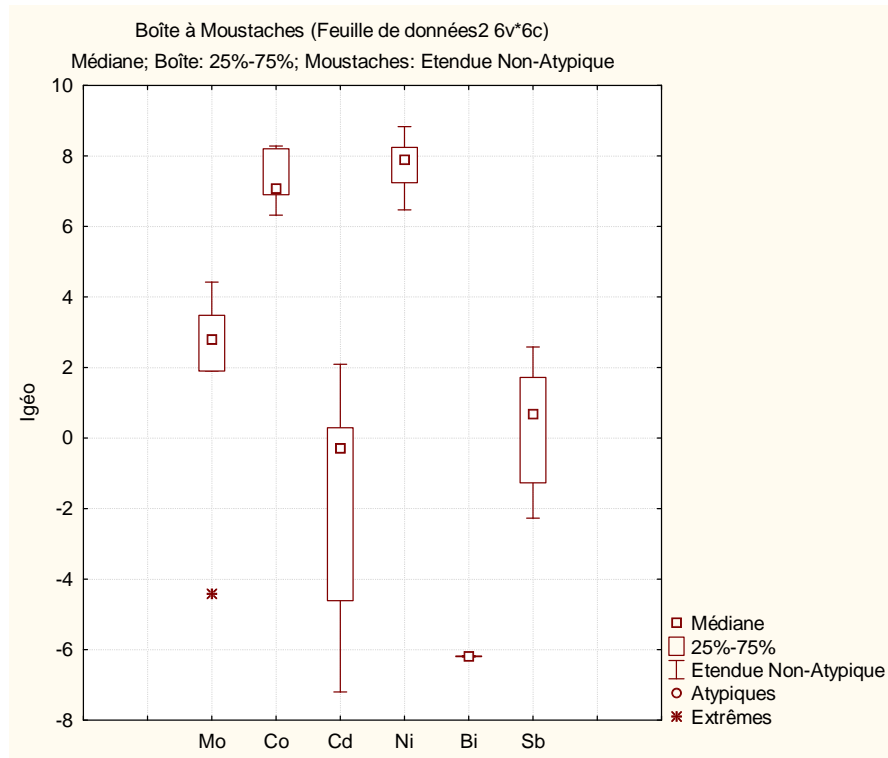


Fig.4: Box plots of the Igeo index for metals

3.4.2. Enrichment factor

The table below shows the enrichment factor results

Table 9: Enrichment factor

	FE						
Stations	Mo	Co	Cd	Ni	Bi	Sb	Fe
S1	0,22	0,12	9,92	0,09	0,10	4,02	1
S2	1,96	0,16	73,83	0,08	0,16	28,18	1
S3	1,39	0,53	28,69	0,21	0,22	5,24	1
S4	0,56	0,30	10,51	0,18	0,13	0,23	1
S5	0,00	0,09	0,43	0,06	0,10	0,23	1
S6	0,44	0,07	0,09	0,03	0,12	0,57	1
Min	0,00	0,07	0,09	0,03	0,10	0,23	1
Max	1,96	0,53	73,83	0,21	0,22	28,18	1
mean	0,76	0,21	20,58	0,11	0,14	6,41	1

The enrichment factor index values of heavy metals in sediments are presented in Table 9. The metals Mo, Co, Ni and Bi in all sites (S1, S2, S3, S4, S5 and S6) are less than 2. This means that these four metals show a low enrichment state in these sediments. Cd in stations S2 and S3 show an extreme enrichment state versus a significant enrichment state in stations S1 and S4. Sb shows a low enrichment state in stations (S4, S5 and S6) and a very high enrichment state in station S2. On

average $FE(Cd) > FE(Sb) > FE(Fe) > FE(Bi) > FE(Mo)$. The figure below shows box plots of metal contamination factors.

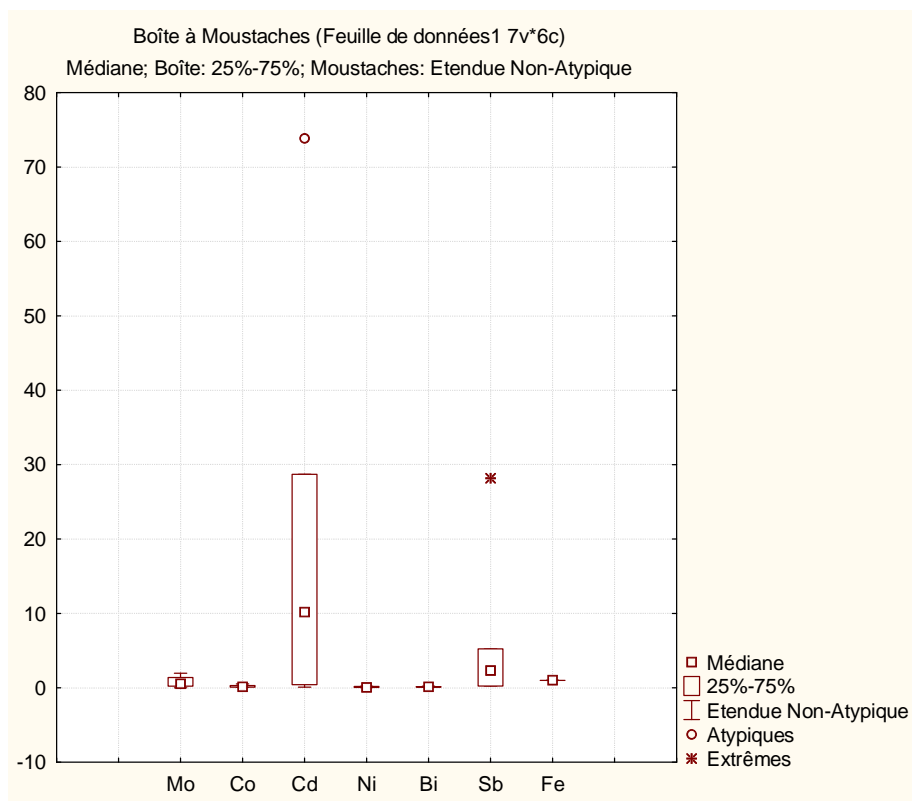


Fig. 5: Box plots of metal contamination factors

3.4.3. Potential ecological risk

The table below shows the Ecological Risk Potential values

Table 10: Potential Ecological Risk

Er						
Stations	Mo	Co	Cd	Ni	Sb	ERI
S1	42,85	7,5	3823,52	5,78	2064,51	5944,19
S2	246,42	6,66	18529,41	3,15	3741,93	22527,60
S3	128,57	16,25	5294,11	6,31	1290,32	6735,57
S4	85,71	15,41	3235,29	9,47	774,19	4120,09
S5	0,53	6,25	3235,29	4,21	129,032	3375,32
S6	75	4,166	29,41	1,84	258,064	368,48
Min	0,53	4,16	29,41	1,85	129,032	368,48
Max	246,42	16,25	18529,41	9,47	3741,93	22527,60
Mean	96,51	9,37	5691,17	5,13	1376,34	7178,54

The potential ecological risk for Ni and Co in all stations $Er < 40$. This reflects a low risk to the environment as well as Mo and Cd in S5 and S6 respectively. Cd and Sb having the values of potential ecological risk is high which reflects a high risk to the environment. On average $Er(Cd) > Er(Sb) > Er(Mo) > Er(Co) > Er(Ni)$.

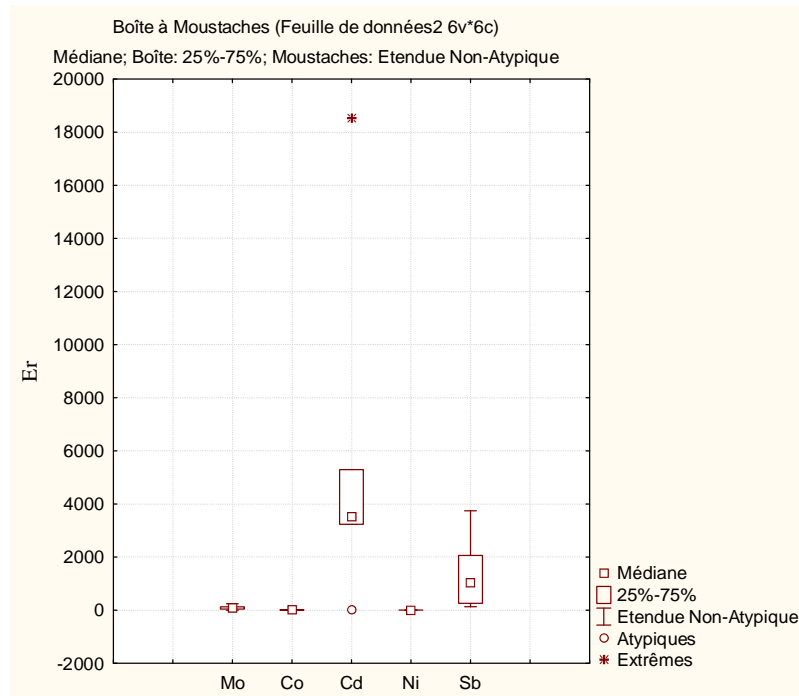


Fig. 6: Box plots of metal contamination factors.

3.5. Factor analysis

The table below represents the eigenvalues of the PCA performed on the sediments of the Mfouati River. This table indicates that the first principal component (axis 1) explains 42.37% of the total variance, the second principal component (axis 2) explains 31.73% of the total variance, for a total of 74.10%. The third principal component (axis 3) explains 14.17% of the total inertia. The fourth principal component explains (axis 4) 7.45% of the total inertia.

Table 11: Inertia rates and eigenvalues of the first 4 axes

Val Propre	% Total variance	Cumul Val propre	Cumul %
5,932084	42,37203	5,93208	42,37203
4,442539	31,73242	10,37462	74,10445
1,984517	14,17512	12,35914	88,27957
1,043032	7,45023	13,40217	95,72980

3.5.1. Factorial design formed F1 and F2

The following elements: LF, Arg, MO occupy the F1 axis. These elements (LF, Arg, Mo) correlate positively with the F1 axis. The following elements LG, pH and SF being close to the center of the factorial plane, their correlation is certainly not very strong. The elements Sb, Cd, CE, As occupy the factorial plane F2, they are strongly correlated between them in a positive way. The figure below shows distribution of the variables in the factorial design F1x F2.

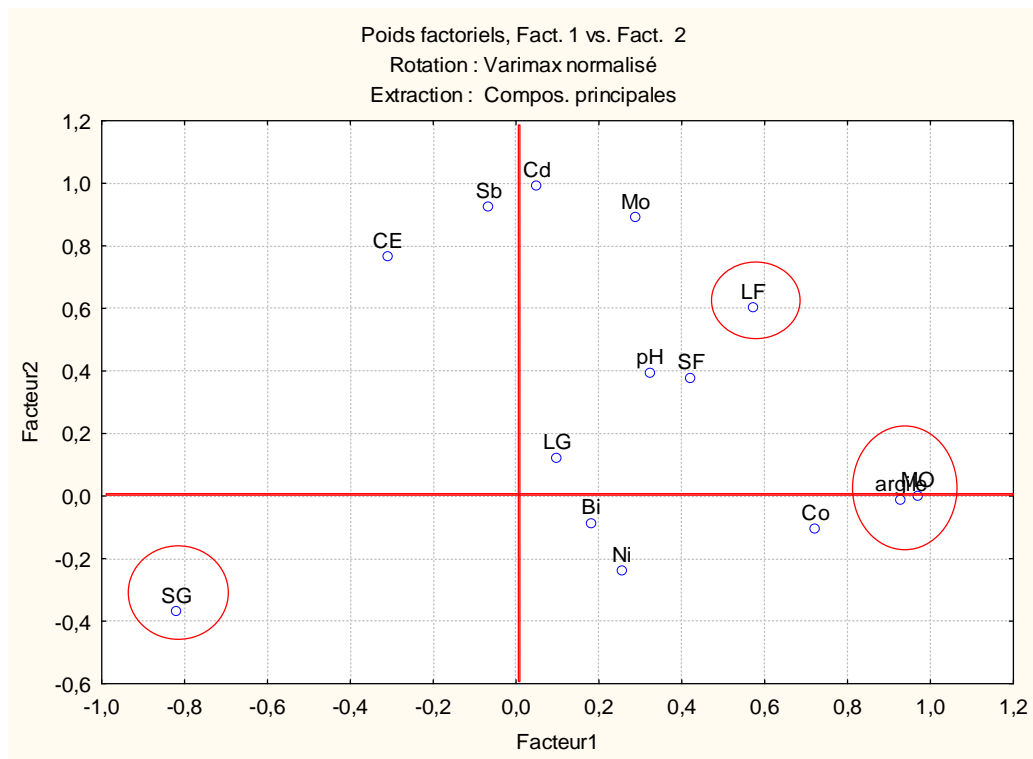


Fig. 7: Distribution of the variables in the factorial design F1 x F2

3.5.2. Factorial design formed F1 and F3

The following elements: Mo, Arg, MO occupy the F1 axis. These elements (Mo, Arg, MO) correlate positively with the F1 axis. The following elements pH, Ni, Mo being close to the center of the factorial plane, their correlation is certainly not very strong. The elements Sb, Cd, CE, As occupy the factorial plane F2, they are strongly correlated between them in a positive way. The figure below shows distribution of variables in the factorial design F1 x F3.

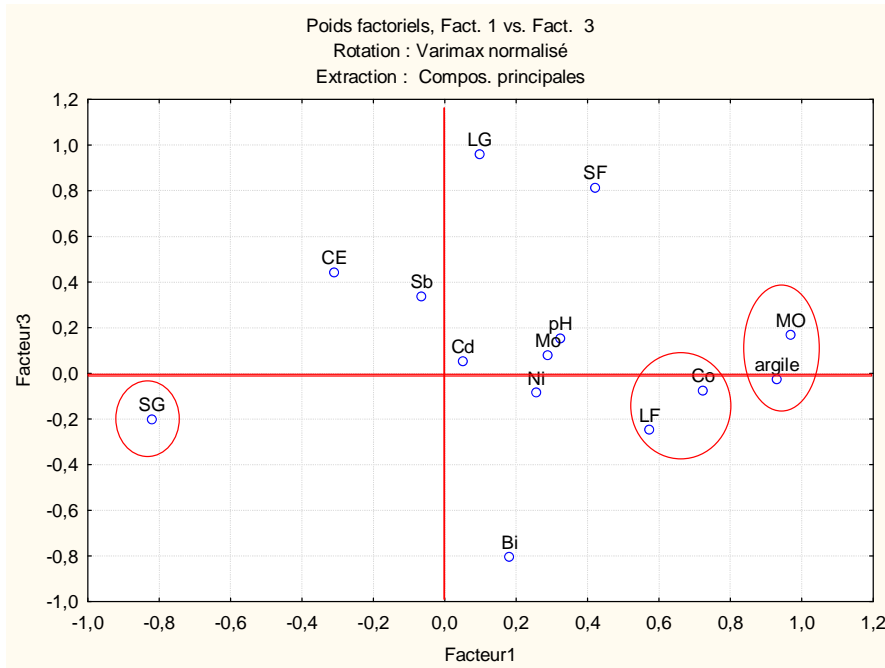


Fig. 8: Distribution of variables in the factorial design F1× F3

3.6. Hierarchical ascending classification

The ward method was used taking into account the Euclidean distance. The figure shows the dendrogram of the stations. This classification resulted in three groups of stations. Group 1 contains stations S1 and S3, group 2 contains stations S2, S4, S5 and group 3 contains station S6. The figure below dendrogram of the stations.

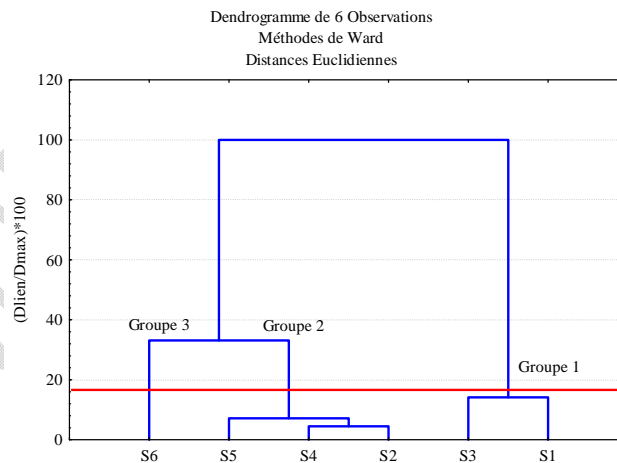


Fig. 9: Dendrogram of the stations

4. Conclusion

The general objective of this work is to know the current status of heavy metal contamination (Mo, Co, Cd, Ni, Sb, Bi) in the sediments of the Mfouati River. The sediments were characterized by particle size analysis using the Robinson pipette method. Organic matter was determined by the black method. Mineralogical analysis was determined by X-ray diffraction. The concentrations of heavy metals (Mo, Co, Cd, Ni, Sb, Bi) were determined in the raw sediments. The level of contamination of

the sediments was evaluated through geochemical indices. The results of this study with regard to the granulometric analysis show that we have a predominance of coarse sand in the sediments of the Mfouati River 59.35% in the station S5. The results obtained show that the physical-chemical parameters (pH, EC and TDS) measured are within the standards (WHO). Only the pH which presents a slightly acidic character at the stations (S4, S5, S6). The results of the mineralogical analysis revealed the presence of the following minerals: talc, potassium, iron. The contents of heavy metals found (mg/Kg) vary between: Mo [0,05-23]; Co:[10-39]; Cd[0,1-63]; Ni[7-36]; Bi[0,164-0,169]; Sb[1-29]. The results of contamination factor showed the following order:FC(Cd)> FC(Sb) >FC(Mo) >FC(Co) >FC(Bi) >FC(Ni);enrichment factor the order is as follows: FE(Cd)>FE(Sb)>FE(Fe) >FE(Bi) >FE(Mo); geo accumulation index the order is as follows:Igeo(Ni)>Igeo(Co) >Igeo(Mo) >Igeo(Sb) >Igeo(Cd) >Igeo(Bi).

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