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Metal Concentrations in Surface Sediments of Tafna Estuary in North-Western Algeria

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Abstract

This paper evaluates the degree of contamination in the Tafna estuary in Rachgoun, (Wilaya of Ain Temouchent, Algeria) through the temporal-spatial monitoring of the content of certain metal elements (Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn) in surface sediments, during the period between October 2009 and March 2010. We focused on the assessment of these metals in order to quantify their impact on the Mediterranean Sea.

The technique used for analysis is the Atomic Absorption Spectrophotometry (AAS) method. The results revealed a relatively low metallic content in sediments, except for cadmium which reached particularly high concentrations and exceeded the background values. Metal levels were higher in January particularly for Co and Zn. The accumulation of heavy metals in surface sediments was derived using geoaccumulation index (I_{geo}) and enrichment factor (*EF*). The results of geoaccumulation index (I_{geo}) reveal that sediments are uncontaminated with Co, Cr, Cu, Fe, Mn; moderately contaminated with Pb and Zn; and moderately to heavily contaminated with Cd. The enrichment factors showed that Co, Cr, Cu, and Mn are depleted whereas Cd, Pb, and Zn are enriched. One-way ANOVA and principal component analysis (PCA) were used to compare the data for different months (0,05).

Keywords: Ain Temouchent, Algeria, Heavy metals, Sediments, Tafna estuary.

I. INTRODUCTION

Estuaries, or freshwater-saltwater interface zones, are areas of great ecological and economic importance. They are among the most exposed zones to different types of pollution, including metal, whether as a direct result of industrialization and urbanization, or as indirect contributions by rivers and the atmosphere. Among the chemical substances often at the source of metal pollution are heavy metals. They are distinguished from other chemical pollutants by their low biodegradability and their large bioaccumulation capacity throughout the trophic chain, which can cause major ecological damage.

Wadi Tafna is 170 km long and is located in the north-western region of Algeria, draining a basin of 7245 km^2. Tafna estuary, the terminal part of wadi Tafna, is located near the beach of Rachgoun (Wilaya of Ain Temouchent), at approximately 30 km west of the town of Ain Temouchent (Fig. 1). This estuary is characterized by the development of basaltic tuff of volcanoes which are present on all its sites. This region has a Mediterranean climate and is characterized by a semi-arid regime of rainfall and temperatures.

This study was carried out to determine the current state of metal contamination in the Tafna estuary (Rachgoun), in order to complete and update previous works on metal pollution in the far west of Algeria and to gain more knowledge on the system of estuaries which is unfortunately not very well developed in our country [1,2]. Indeed, it was interesting to measure the heavy metal pollution levels of surface sediments of Tafna estuary by working out the temporo-spatial distribution of eight metals (Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn) during the period between October 2009 and March 2010. Subsequently, a correlation was established between the sites, months and contamination. The purpose of this correlation is to explain the phenomenon of heavy metal supply to sediments. The description of these variations is beyond the scope of the paper.

II. Materials and methods

2.1. Sampling, Sample Treatment and Analysis

Sampling was carried out monthly between October 2009 and March 2010. Four sampling points were selected along the estuary (Fig.1).

A is located on the estuary part the most affected by the sea. B is located 100 m away from point A and C 200 m away from the same point (close to the uncontrolled dump site). Its survey will allow us to see the impact of domestic waste on the contamination of estuarine sediments. D is located at 400 m from point A.

The surface sediments (the first five centimeters) were scraped with a small spade, stored in transparent plastic bags, labeled and transported to the laboratory in a cooler at 4 °C. Then, they were dried in ambient air for a few days. The samples were pre-sieved (2 mm) to eliminate shell, branch and leaf fragments, and crushed using a porcelain mortar to obtain a fine powder, followed by separation through a sieve to obtain the lower fraction (i.e.: < 63 µm). This fraction represents more than 95 % of the sediments (granulometric analyses by CILAS 850 granulometer). The lower fraction is kept and mineralized with a mixture of acids of HCl + HNO_3 (volume ratio of 3:1) in Teflon flasks at 120 °C. The protocol of mineralization used in our investigation was proposed by [3, 4]. The resulting solutions were filtered with a 0,45 µm filter (natural absorbing membrane), filled to 20 ml with bi-distilled water [5] and kept at 4 °C until analysis. Acids exhibiting high purity were employed, i.e. HCl and HNO_3, from Merck Suprapur quality.

A flame atomic absorption spectrophotometer type IA AURORA 1200 was used to determine the eight metals Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn. All data were computed on a milligram per kilogram dry weight basis. The accuracy of the analytical procedures for total metal determinations was checked using MESS (1) (certified standards) provided by the National Research Council of Canada. This was analysed under the same experimental conditions. Replicate analysis of these reference materials showed good accuracy with recovery rates for metals around 96 %**.** The absorption wavelengths were 228,8 nm for Cd, 240,7 nm for Co**,** 357,9 nm for Cr, 324,7 nm for Cu, 248,3 nm for Fe, 278 nm for Mn, 283,3 nm for Pb, and 213,9 nm for Zn. For each sampling point, six total digestions were performed and the overall value was recorded as the average of these tests with their respective standard deviations.

2.2. Geoaccumulation index and enrichment factors

2.2.1 Geoaccumulation index (I_{geo})

A common approach to estimating the enrichment of metal concentrations above background or baseline concentrations is to calculate the geoaccumulation index (I_{geo}) as proposed by Müller [6]. The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows:

$$I_{geo} = Log2 (C_n / 1,5 B_n)$$

Where C_n is the concentration of the element in the enriched samples, and B_n is the geochemical background concentration of metal n. The factor 1,5 is introduced to minimize the effect of possible variations in the background values, which may be attributed to lithologic variations in sediments [7]. The geoaccumulation index consists of seven grades or classes [6]. Class 0 (practically uncontaminated): $I_{geo} < 0$; class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated): $0 < I_{geo} < 2$; class 3 (moderately to heavily contaminated): $2 < I_{geo} < 3$; Class 4 (heavily contaminated): $3 < I_{geo} < 4$; Class 5 (heavily to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $5 < I_{geo}$. Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentration in Class 6 may be hundredfold greater than the geochemical background value.

2.2.2 Enrichment factor (EF)

It is common to estimate the anthropogenic impact on sediments by calculating a normalized enrichment factor *(EF*) for metal concentrations above uncontaminated background levels [8, 9]. The *EF* calculation seeks to reduce the metal variability associated with variations in mud/sand ratios, and is a convenient tool for plotting geochemical trends across large geographic areas, which may have substantial variations in the mud (i.e. clay rich) to sand ratios.

This method consists in using a reference element of terrigenous origin, mainly Al, Fe or Si (known as terrigenous metals) to determine the terrigenous portion of metal contribution [10, 11]. If the *EF* is higher than one, it may be indicative that the sediment is of an anthropogenic source and can be used for assessing the degree of pollution.

For our study, the enrichment factor of the sediments was calculated by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline (Taylor, 1964). Thus, *EF* is computed using the relationship below:

$$EF = (Me / Fe)_{Sample} / (Me / Fe)_{Background}$$

Where *EF* is the enrichment factor, $(Me/Fe)_{Sample}$ is the ratio of metal and Fe concentration of sample, and $(Me/Fe)_{Background}$ is the ratio of metal and Fe concentration of a background. Many authors prefer to express the metal contamination with respect to average shale to quantify the extent and degree of metal pollution ([6, 12]. In this study, the background concentrations of Cd, Co, Cr, Cu, Mn, Pb, and Zn were taken from [13].

The advantage of using the enrichment factor *(EF*) analysis is that it allows establishing a contamination guideline. This technique has been well applied in several studies to assess metal contamination in marine sediments [14-19]. Where $EF < 1$ indicates no enrichment; $1 < EF < 3$ indicates minor enrichment; $3 < EF < 5$ indicates moderate enrichment; $5 < EF < 10$ indicates moderately severe enrichment; 10 < *EF* < 25 indicates severe enrichment; 25 < EF < 50 indicates very severe enrichment; *EF* > 50 indicates extremely severe enrichment. Rubio et al., [20] recommended the use of regional background values. While the geochemical background values are constant, the levels of contamination vary with time and places.

2.3. Statistical Methods

Statistical analysis was performed using XLSTAT software. One-way ANOVA test was used to compare the data for different months at the level of 0,05 and also a multivariate analysis of the results was done using principal component analysis (PAC) on the mean metal concentrations in sediments.

III. Results and discussion

3.1. Absorption analysis

Figure 2 exhibits average results concerning the elements Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn obtained monthly from a large number of samples analyzed by SAA. It represents the temporal variations. The horizontal lines in each one of the figures indicate the average international values specific for each element given by (IAEA-405) (International Atomic Energy Agency) [21]. The calculated standard deviations do not show a large variability, which is satisfactory for the purpose of this study.

The results for cadmium indicate a very important accumulation, easily exceeding the average reference level for estuarine sediments (IAEA-405) [21], which is found to be around 0,73 mg/kg, at the four points A, B, C and D. This contamination may be related to the use of cadmium found in batteries, in plating for protecting steel against corrosion, in plastics and pigment stabilization. It could also be attributed to agricultural activities that make use of phosphate compounds with large amounts of cadmium [22]. The month of January exhibits the highest metal concentrations (Fig. 2). The amount of domestic sewage emanating from the surrounding cities is directly discharged into the estuary. These factors may explain the high levels of Cd found in surface sediments. [23] established average Cd concentrations in the world from 1,5 to 7,7 mg/kg with maximum values closest to industrial complexes and sewage pipelines. Atmospheric deposition may also contribute to Cd enrichment in sediments [24, 25]. Concentrations of Co and Zn are high during the month of January and exceed the standard background for site D.

The monthly average Cd concentrations in all sites ranged from A to D (A < B < C < D) and exceeded the IAEA-405 standard values. For the other metals, the monthly average concentrations were lower than the shale.

Tafna estuarine sediments were characterized by a strong presence of all metals under investigation during the month of January (a rainy period). This reveals the low metal contents released during this period. The low metal content of sediments from February onwards could be explained by the phenomenon of dilution. The same observations were made at the four sampling stations. The results of the current study show that, the concentrations of all elements were significantly high (P < 0,005) from one month to another (ANOVA 1).

Table 1 shows the average concentrations (± S.D.) (mg/kg dry weight) of Cd, Cu, Cr, Cu, Mn, Pb and Zn, (mg/g dry weight) of Fe in the sediments with I_{geo} index values, and enrichment factors *EF* at the four stations (A, B, C and D). Figure 3 shows the spatial variations of averages of metal concentrations at the four study sites.

Cr, Cu, Fe, Mn and Pb concentrations vary slightly from one point to another, but do not exceed the international values (IAEA-405).

The average metal content of Tafna estuarine sediments was found in order of Fe > Mn > Zn > Cr > Pb > Co > Cd, for sites: D > C > B > A.

The overall results show that the sampling points C and D, which drain the discharge of domestic wastewater and are located near the uncontrolled dump, exhibit significant contamination. Conversely, the two other points A and B, influenced by the marine environment, show less pollution. The results of the current study show that, with the exception of Cd, Fe and Mn levels (P > 0,05), concentrations of most elements were significantly high from one site to the next one (ANOVA 1).

Cadmium presented the highest levels (Fig 3); however it shows very high toxicity to both aquatic and terrestrial organisms even at low concentrations [26]. For dissolved cadmium, acute LC 50 values as low as 3,5 µg/l have been reported for planktonic organisms [27]. Although Cd is a sulfur seeking metal that tends to precipitate in anoxic sediments, experiments carried out at concentrations close to or lower than the values found in this study, showed that they can be considered as anoxic sediments with high organic matter content [28-30]. Therefore, they can potentially bioaccumulate through dietary uptake.

3.2. Geoaccumulation index and enrichment factors

The geoaccumulation index can be used as a reference to estimate the extent of pollution processes. The geoaccumulation index averages for the sampling stations and for all metals are shown in table 1. According to Müller scale [6], used by other authors, i.e. [31], all sampling stations are classed between 0 and 2, corresponding to uncontaminated to moderately contaminated. Then, they are subjected to polluting effects. Co, Cr, Cu, Fe and Mn exhibit average I_{geo} values that correspond to an unpolluted situation. Cadmium can be considered as a moderate pollutant in all stations (I_{geo} = 1,80).

The results of the present study show a high Cd index in sediments at sites A and B (5 < FE < 10), and it is higher in sediments at sites C and D (10 < FE < 25) (Table 1). Pb and Zn are moderately high in sediments at both sites C and D. These findings are consistent with the remarks made earlier about these elements (Fig. 2). The highest average *EF* is seen for Cd with a value of 10,81. Lead has the second highest *EF* with an average value of 4,10, followed by zinc with an average value of 3,33 (Table 1). This suggests that Cd, Pb and Zn originate from anthropogenic inputs including fertilizers and pesticides used in agricultural activities. The difference in *EF* values may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediment.

Average sediment concentrations for all metals in our study and for other estuaries are given in Table 2. Mean metal concentrations were generally comparable with the ones found in the four Moroccan estuaries; except for Cu, Fe, Mn, and Zn which were lower in our study. Pb and Zn concentrations exceeded the ones found in [2]). Cd and Pb concentrations exceeded the background values [13].

3.3. Factor analysis

In order to study inter-elemental associations, the correlation coefficients of the elements analyzed were computed for all sediment samples. The total concentration data were also subject to factor analysis to identify estuary sediment sources.

The principal component analysis (PCA) gives us 83,2 % of information. Variance information gives 75,3 % for factor 1 and 7,9 % for factor 2. Figure 4 shows that the variables have high positive loadings on factor 1. On the other hand, the variables of Cd, Cr, Mn, Pb, and Zn have high positive loadings on factor 2. Two factors with different factor loadings indicate that two different contributions are involved in determining the heavy metal concentrations in estuarine sediments.

IV. Conclusion

Based on our results, sediments from Tafna estuary show that only cadmium exceeds the average reference of 0,73 mg/kg for all stations and months. Co and Zn exceed reference values in January for station D. The month of January presents the highest metal concentrations.

The impact of anthropogenic heavy metal pollution in Tafna estuary was evaluated using the geoaccumulation index (I_{geo}) and the enrichment factor (*EF*), for Cd, Co, Cr, Cu Mn, Pb and Zn at four stations.

The geoaccumulation indices (I_{geo}) are distinctly variable and suggest that sediments in Tafna estuary range from uncontamined to moderately contaminated with respect to metal analysis. The uncontamination I_{geo} designation is clearly supported by other methods for calculating the metal pollution impact in Tafna estuary.

Normalized enrichment factor (*EF*) values for seven heavy metals were calculated for Tafna estuary using the continental shale abundance of Fe. The results showed higher average *EF* values for Cd (10,83), followed by Pb (4,10), and by Zn (3,33). These findings are consistent with the remarks made earlier for these elements. The values of the enrichment factor of the sampling points and metals are somewhat high (table 1). Overall, the average enrichment factor *EF* was between 1 and 5 but never exceeds 10, which excludes the case of severe enrichment. The element whose enrichment is most critical at present is cadmium. The averaged pollution degree of cadmium in C and D sampling sites.

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Figures and Tables Captions

Figure Captions

Figures:
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Figure 2: Temporal variations of average metal concentrations (Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn) in surface sediments of the Tafna estuary
Figure 3: Spatial variations of average concentrations of metals (Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn) in surface sediments of the Tafna estuary
Figure 4: Biplots for first and second axis of the PAC bases on mean values of metal concentrations (Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn) in months and stations of the Tafna estuary

Tables:
Table 1: Average concentrations (± S.D.) (mg/kg dry weight) of Cd, Cu, Zn and Pb in sediments with I_{geo} index values, and enrichment factors (*EF*) at the four stations (A, B, C and D)
Table 2: Comparison with literature and background values (mean ±SD, mg/kg dry weight, except Fe in mg/g).

Figure 1:

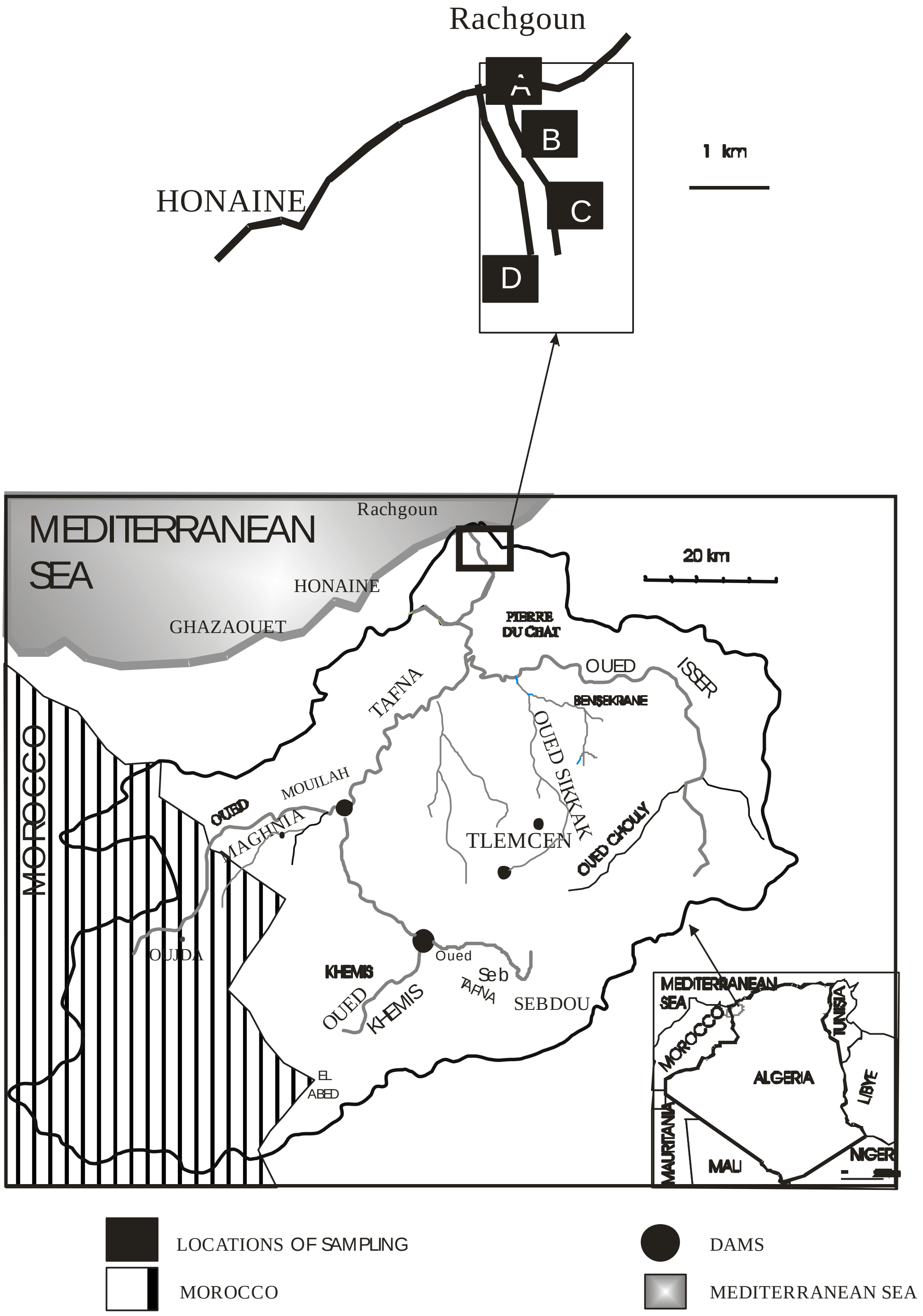
Rachgoun
A
B
C
D
HONAINE
1 km
MEDITERRANEAN SEA
Rachgoun
HONAINE
GHAZAOUET
20 km
PIERRE DU CHAT
OUED ISSER
BENISEKRANE
TAFNA
OUED SIKKAK
MOUILAH
OUED MAGHNIA
TLEMCEN
OUED CHOULY
MOROCCO
OUJDA
KHEMIS
Oued
Seb
TAFNA
SEBDOU
OUED KHEMIS
EL ABED
MEDITERRANEAN SEA
MOROCCO
TUNISIA
ALGERIA
LIBYE
MAURITANIA
MALI
NIGER
■ LOCATIONS OF SAMPLING
● DAMS
MOROCCO
MEDITERRANEAN SEA

Figure 2:

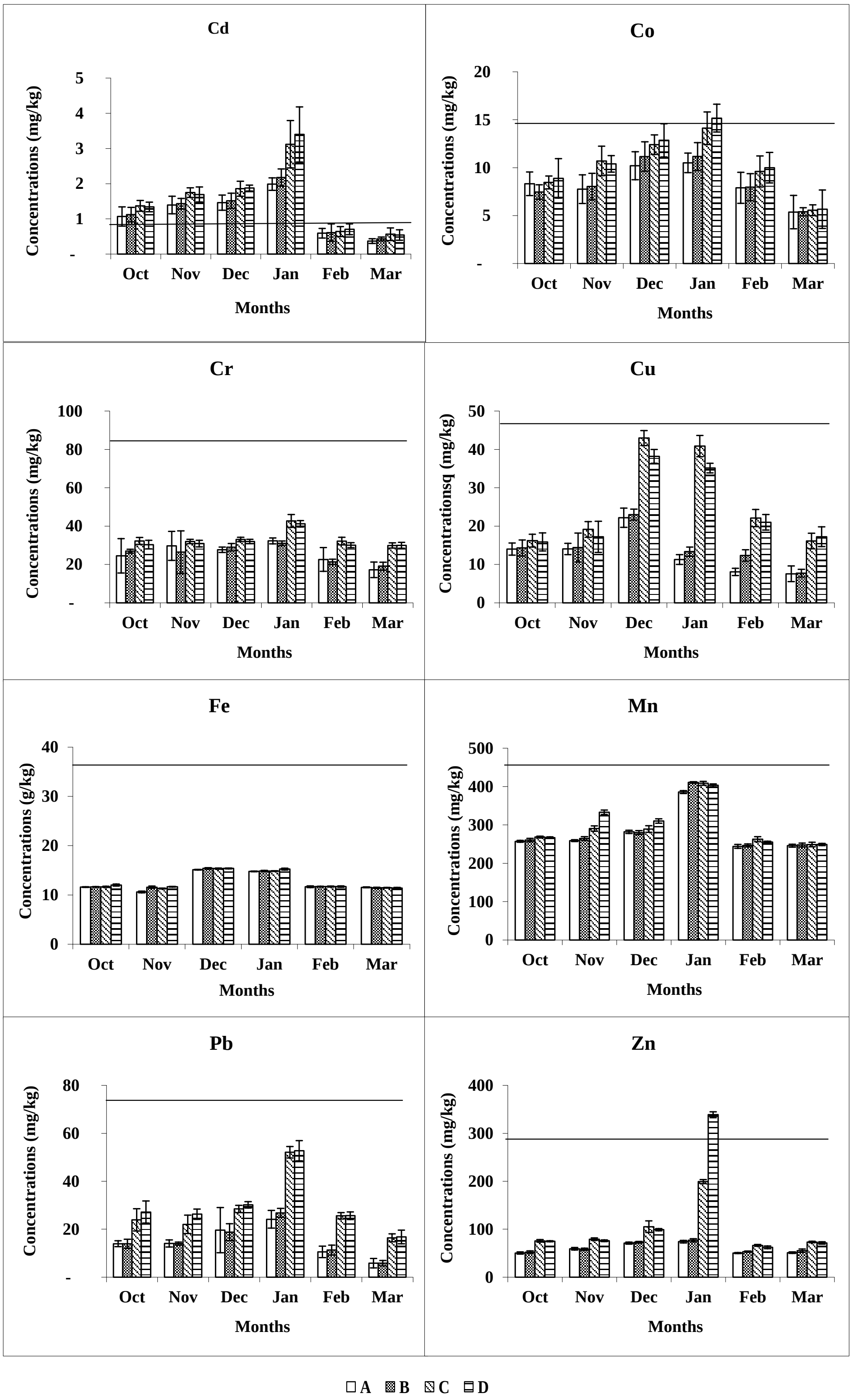
Cd
Concentrations (mg/kg)
5
4
3
2
1
-
Oct
Nov
Dec
Jan
Feb
Mar
Months
Co
Concentrations (mg/kg)
20
15
10
5
-
Oct
Nov
Dec
Jan
Feb
Mar
Months
Cr
Concentrations (mg/kg)
100
80
60
40
20
-
Oct
Nov
Dec
Jan
Feb
Mar
Months
Cu
Concentrationsq (mg/kg)
50
40
30
20
10
0
Oct
Nov
Dec
Jan
Feb
Mar
Months
Fe
Concentrations (g/kg)
40
30
20
10
0
Oct
Nov
Dec
Jan
Feb
Mar
Months
Mn
Concentrations (mg/kg)
500
400
300
200
100
0
Oct
Nov
Dec
Jan
Feb
Mar
Months
Pb
Concentrations (mg/kg)
80
60
40
20
-
Oct
Nov
Dec
Jan
Feb
Mar
Months
Zn
Concentrations (mg/kg)
400
300
200
100
0
Oct
Nov
Dec
Jan
Feb
Mar
Months
☐A ▦B ▧C ▤D

Figure 3:

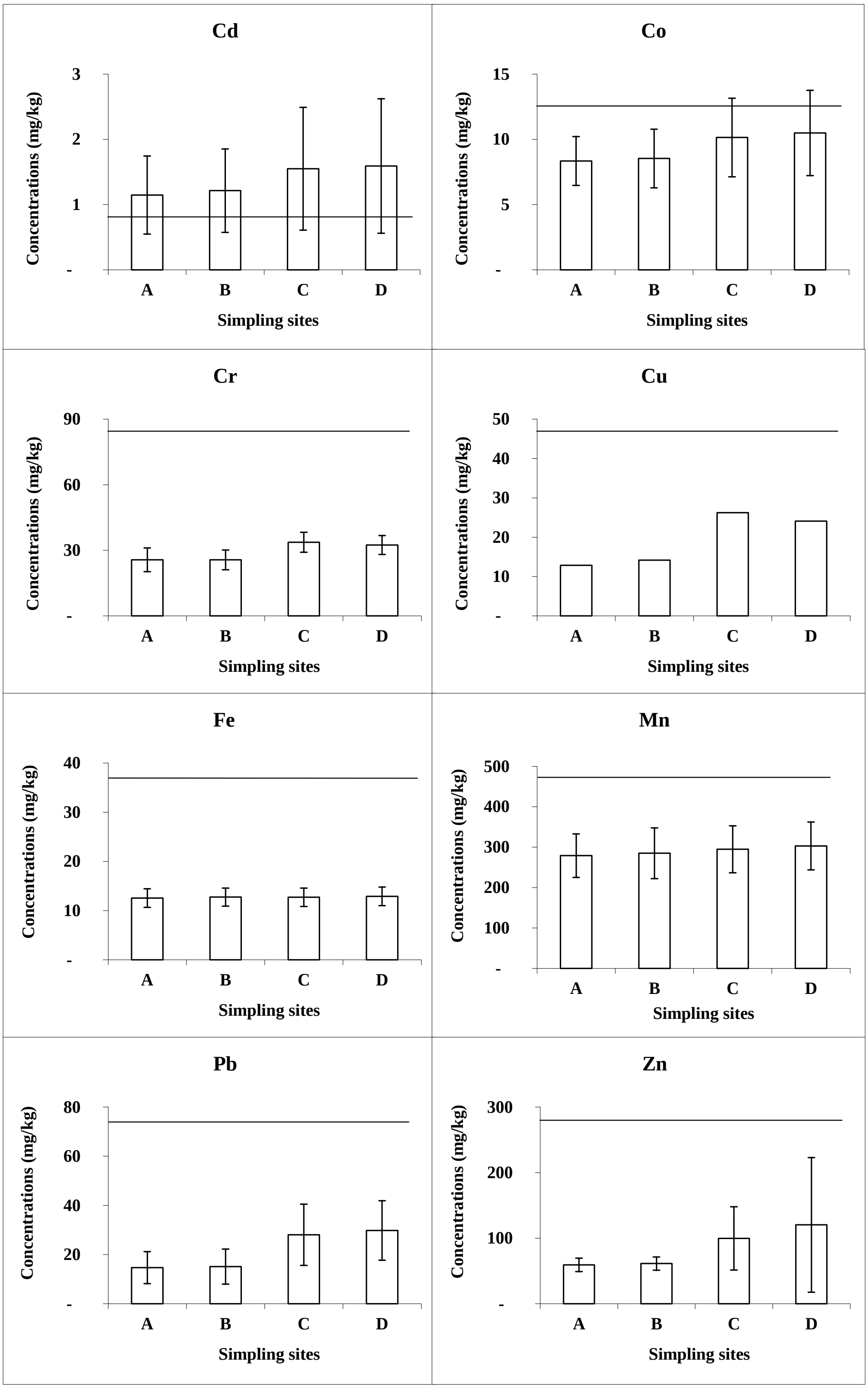
Cd
3
2
1
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Co
15
10
5
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Cr
90
60
30
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Cu
50
40
30
20
10
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Fe
40
30
20
10
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Mn
500
400
300
200
100
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Pb
80
60
40
20
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites
Zn
300
200
100
-
A
B
C
D
Concentrations (mg/kg)
Simpling sites

Figure 4:

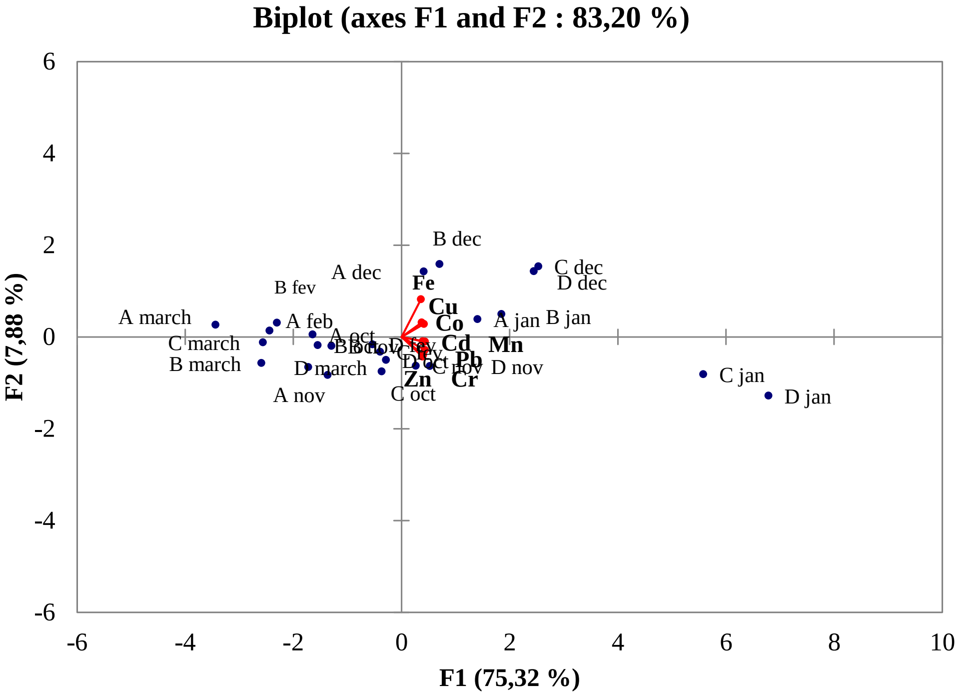

Table 1:

Station	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
A	1,14 ± 0,59	8,34 ± 1,87	25,67 ± 5,42	12,86 ± 5,35	12547,44 ± 1900	278,97 ± 53,00	14,68 ± 6,48	59,28 ± 10,3
B	1,21 ± 0,64	8,53 ± 2,25	25,64 ± 4,54	14,18 ± 4,97	12757,69 ± 1840	284,98 ± 62,87	15,08 ± 7,13	61,29 ± 10,18
C	1,55 ± 0,94	10,14 ± 3,01	33,68 ± 4,55	26,23 ± 12,36	12712,68 ± 1860	294,71 ± 57,99	28,08 ± 12,45	99,75 ± 48,22
D	1,59 ± 1,03	10,49 ± 3,27	32,42 ± 4,36	24,11 ± 9,93	12894,97 ± 1880	302,93 ± 59,19	29,79 ± 12,11	120,32 ± 102,6
Average	1,38 ± 0,22	9,38 ± 1,09	29,35 ± 4,30	19,34 ± 6,80	12728,2 ± 143,29	290,39 ± 10,57	21,91 ± 8,14	85,16 ± 29,93
Turekian and wedpohl shale	**0,3**	**19**	**90**	**45**	**47200**	**850**	**20**	**95**

I_{geo}	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
A	1,63	-0,54	-0,97	-0,96	-1,04	-0,83	-0,02	-0,18
B	1,68	-0,51	-0,97	-0,87	-1,02	-0,81	0,01	-0,15
C	1,93	-0,34	-0,70	-0,25	-1,02	-0,77	0,63	0,34
D	1,96	-0,31	-0,73	-0,34	-1,01	-0,74	0,69	0,52
Average	**1,80**	**-0,42**	**-0,84**	**-0,61**	**-1,02**	**-0,79**	**0,32**	**0,13**
Class	**2**	**0**	**0**	**0**	**0**	**0**	**0-1**	**0-1**
	moderately contamination	uncontaminated	uncontaminated	uncontaminated	uncontaminated	uncontaminated	uncontaminated to moderately contamination	uncontaminated to moderately contamination

EF	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
A	9,13	1,66	1,07	1,08	-	1,23	2,78	2,35
B	9,51	1,67	1,05	1,17	-	1,24	2,81	2,39
C	12,19	1,99	1,39	2,17	-	1,29	5,26	3,90
D	12,41	2,04	1,32	1,98	-	1,31	5,53	4,67
Average	**10,81**	**1,84**	**1,21**	**1,60**	-	**1,27**	**4,10**	**3,33**
	sever enrichment	minor enrichment	minor enrichment	minor enrichment	- -	minor enrichment	moderate enrichment	moderate enrichment

Table 2:

Estuaries	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
Tafna Estuary Dali youcef et al., [2]	-	-	52,6 ±6,9	23,8 ± 0,6	29,70 ± 1,10	323 ± 7	20,4 ± 0,6	60,2 ± 4,1
Loukoss estuary Cheggour et al., [1]	1,34 ± 0,49	-	-	32,4 ± 6,8	20,8 ± 4,1	53,3 ±20,5	-	131 ± 9
Sebou estuary Cheggour et al., [1]	2,3 ± 0,7	-	-	51,5 ± 12,0	29,2 ± 2,1	117 ± 26	-	179 ± 24
Bou Regreg estuary Cheggour et al., [1]	2,3 ± 0,7	-	-	45,2 ± 9,0	33,7 ± 2,5	144 ± 22	-	172 ± 14
Oum Rbia estuary Cheggour et al., [1]	2,7 ± 0,5	-	-	35,2 ± 5,2	14,0 ± 4,6	101 ± 53	-	173 ± 38
Our results	1,38 ± 0,22	9,38 ± 1,09	29,35 ± 4,30	19,34 ± 6,80	12,72 ± 0,143	290,39 ± 10,57	21,91 ± 8,14	85,16 ± 29,93
Background values (Turkian and Wedpool) [13]	0,3	19	90	45	47	850	20	95