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The effect of flood on metal concentrations in sediments, case of the Sebou Estuary, Morocco

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Abstract

This work aims to characterize the chemical composition along the Sebou Estuary in the Kenitra region in Morocco following floods. Surface sediment samples were collected in April 2009, about 2 months after a flooding event. The concentrations of eleven elements (Fe, Mg, Mn, Co, Cr, Cu, Zn, Pb, As, Sr and V) were analyzed by Inductively Coupled Plasma-Quadrupole Mass Spectrometry. The results obtained make it possible to see that the chemical compositions present a negligible variation between sampling sites. The comparison with the quality standards makes it possible to distinguish two sources of pollution: natural (respect of quality standards) and anthropic (exceeding quality standards), the use of the correlation matrix and Principal Component Analysis (PCA) has also identified a third source of mixed pollution. comparison with similar works as well as the application of PCA clearly show the strong relationship with floods that have occurred in the region in the winter of 2009, in particular on Mn (which is experiencing a strong increase following the leaching of soil and traces elements (low concentrations probably due to their transport by suspended particles), this is confirmed by the calculation of contamination factors.

Keywords: Sebou Estuary, major and trace elements, flood, quality standard, comparison, contamination factors, correlation matrix, Principal Component Analysis (PCA).

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1. Introduction

Sediments are complex and heterogeneous environments consisting of water (up to 80%), chemical elements qualified as major (Si, Al, K, Ca, Fe, Mg, etc.) and whose contents are notably related to the geochemical nature of the sediment (detrital, bedrock, etc.), metallic elements present, naturally or due to human activities, in the form of traces (Cr, Cu, Hg, Ni, Pb, Zn, etc.) as well as organic and inorganic contaminants [1].

Sediments have an important role to play in the ongoing monitoring of the environment as they are considered the final reservoir of most terrigenous and anthropogenic sources.

In the last years. The contribution of anthropogenic sources to the enrichment of sediments has increased significantly. The river bank or beaches of many aquatic ecosystems have become urban and industrial, causing high deposits of trace metals [2].

Concerning Sebou Estuary, a zone of great socio-economic importance, the existence of agricultural areas not far from its river bank and the multitude and diversity of industrial units, without forgetting the uncontrolled dumping of household waste are the main causes of degradation of the quality of this Oued.

The purpose of this study was to determine the concentrations of major and trace elements in surface sediment samples to be able to identify the origin of pollution that may be natural or anthropogenic with a statement of flood impact by comparing the results obtained with previous or similar work.

2. Materials and methods

The city of Kenitra is located 40 km north of the capital of the Kingdom of Morocco. It is bounded by Forest Maâmoura in southwest, Lake Fouarat in the east and the Sebou River in the north. The Sebou River is one of the largest Moroccan rivers, draining approximately 40,000 km^2 between 33-35 °N and 4-7 °W. It stretches about 600 km from its source in the Middle Atlas to the Atlantic Ocean [3].

In this work, five sampling sites have been chosen along the Sebou Estuary during low tide as shown in Figure 1.

Surface sediment samples were collected in labeled plastic bags on April 2009 two months from floods at Sebou Estuary. Metal concentrations (Fe, Mg, Mn, Co, Cr, Cu, Zn, Pb, As, Sr and V) were determined by Inductively Coupled Plasma-Quadrupole Mass Spectrometry (Agilent 7500c ICP-Quadrupole MS), following microwave-assisted digestion based on the US EPA 3050 method [4], as modified by [5]. More details are cited in [6].

The principle of ICP-MS (Figure 2) is based on the ionization of the samples in liquid form at ambient pressure thanks to a plasma of neutral gas (argon) generated and maintained by a high frequency electromagnetic field. The choice of argon as a gas is linked to its high ionization potential of 15.8 eV, making possible the total ionization of the majority of the elements of the periodic table.

The sample in liquid form to be analyzed is dispersed in a gaseous stream (argon) and injected inside the plasma at very high temperature (about 7000 K). The energy transferred from the plasma to the sample causes the dissociation of the sample, then its atomization and at the end its ionization.

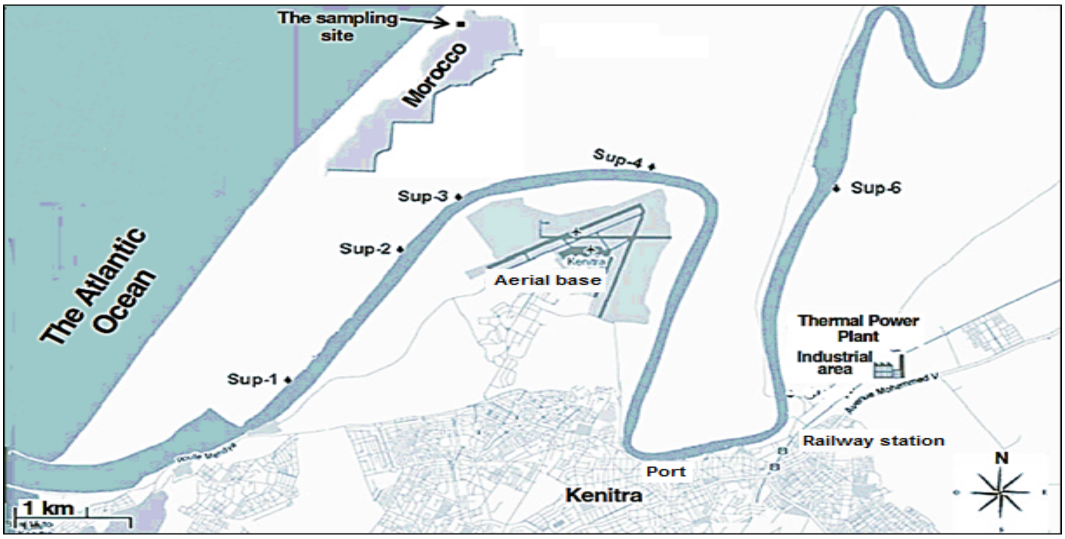

Fig 1. Location map of sampling sites along Oued Sebou in the Kenitra region.

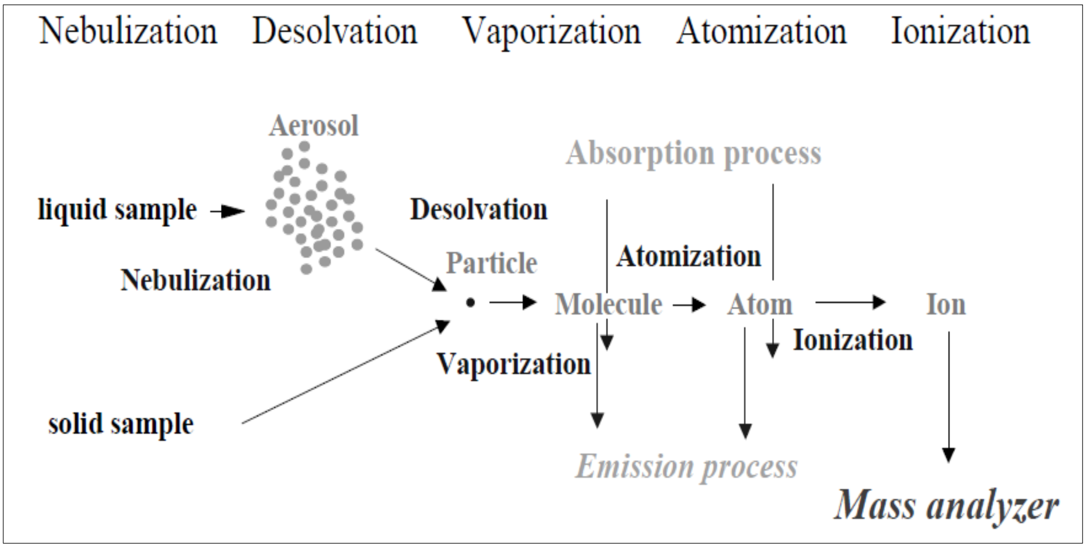

Fig 2. Operating principle of ICP-MS.

3. Results and discussion

3.1. Heavy metal content

3.1.1. Results

Table 1 lists the concentrations of 11 chemical components (Fe, Mg, Mn, Co, Cr, Cu, Zn, Pb, As, Sr and V) in five surface sediment sampling sites (SUP-1, SUP-2, SUP-3, SUP-4 and SUP-6) along the Oued

Sebou in the Kenitra city, as well as some statistical parameters and the comparison with global averages of the chemical components in river sediments.

Table 1. Contents of chemical components for the 5 sampling sites with some statistical parameters and the global averages of the chemical components in river sediments.

Elements concentrations		Fe	Mg	Mn	Sr	Zn	Cr	V	Pb	Cu	Co	As
		mg/g			µg/g							
Samples	SUP- 1	38	14	4	243	98	78	73	20	22	15	5
	SUP- 2	36	16	5	375	93	88	74	17	19	14	5
	SUP- 3	38	16	5	323	93	92	83	19	20	14	7
	SUP- 4	37	15	4	279	160	80	71	25	22	14	7
	SUP- 6	33	13	5	318	76	61	57	15	9	14	5
Statistical parameters	Minimum	33	13	4	243	76	61	57	15	9	14	5
	Maximum	38	16	5	375	160	92	83	25	22	15	7
	Average	**36**	**15**	**4**	**308**	**104**	**80**	**71**	**19**	**18**	**14**	**5**
	Coefficient of variation	6	8	10	16	31	15	13	20	29	4	22
Quality standars [7]		48	-	1.5	150	250	100	170	100	100	20	5

In general, concentrations of all elements in the five stations showed negligible variations, except for Zn and Cu concentrations where the variation coefficients exceed 25%; this is due to the maximum concentration obtained at SUP 4 site for Zn (160 µg/g) and the minimum concentration for Cu at the SUP 6 site (9 µg/g). Also, Fe, Mg and Mn are the most dominant elements; they showed the highest mean concentrations in all sites (given with mg/g) followed in this order by Sr, Zn, Cr, V, Pb, Cu, Co and As (in µg/g).

Compared to the global average of chemical components (Table 1) in river sediments [7], we observe respect of the chemical elements of quality standards for Fe, Mn, Sr, Co and As. While for Zn, Cr, V, Pb, quality standards exceedance is significant.

In order to better illustrate the results of Table 1, the variation profiles of the contents of chemical components are presented in Figure 2.

To be more precise, we will calculate the Contamination Factor (Table 2). This Factor is calculated in relation with a standard reference value by the equation 1 (Eq.1) [8, 9]:

$$CF_i = C_i / Norm_i, \qquad \text{(Eq.1)}$$

with C_i is our concentration for element i, and $Norm_i$ is quality standard for the same element.

For Zn, V, Pb and Cu, the factor ($CF_i < 1$) indicates the absence or low contamination or pollution. For Fe, Sr, Cr, Co and As, the anthropogenic contamination is moderate ($1 \leq CF_i < 3$), whereas for Mn, pollution or contamination is considerable ($3 \leq CF_i < 6$) [10, 11].

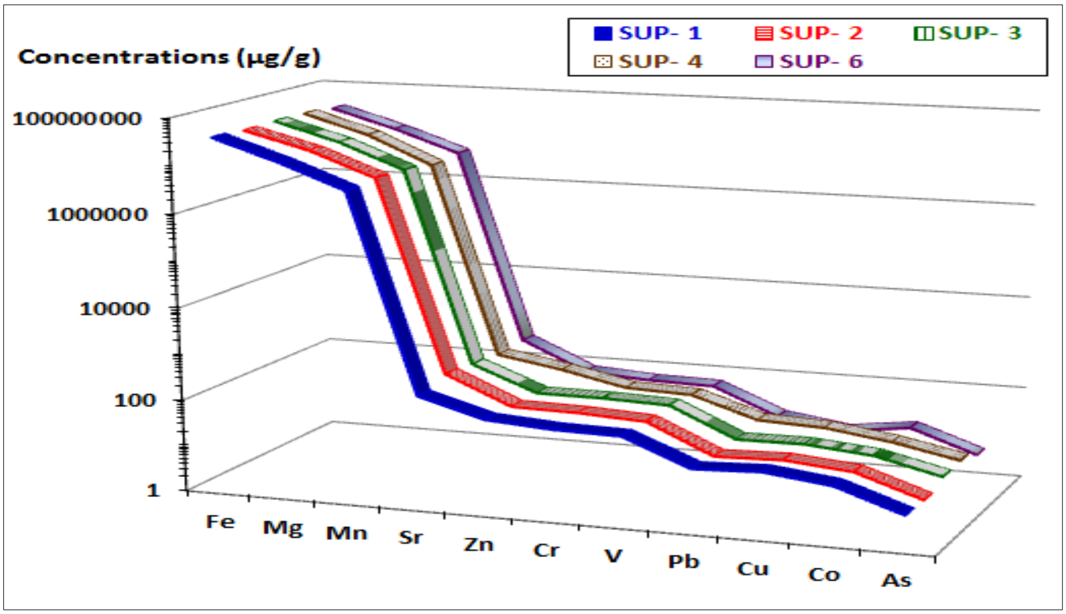

Fig 2. Chemical component profiles for each sampling sites.

Table 2. Contamination factor for the 5 sampling sites.

Contamination Factor (CF)	Fe	Mn	Sr	Zn	Cr	V	Pb	Cu	Co	As
	mg/g		µg/g							
SUP- 1	0.8	2.7	1.6	0.4	0.8	0.4	0.2	0.2	0.8	1.0
SUP- 2	0.8	3.3	2.5	0.4	0.9	0.4	0.2	0.2	0.7	1.0
SUP- 3	0.8	3.3	2.2	0.4	0.9	0.5	0.2	0.2	0.7	1.4
SUP- 4	0.8	2.7	1.9	0.6	0.8	0.4	0.3	0.2	0.7	1.4
SUP- 6	0.7	3.3	2.1	0.3	0.6	0.3	0.2	0.1	0.7	1.0

The comparison of our results with similar works in national and international regions is given by the Table 3. We can see that Fe, Mg and Co present almost the same order of magnitude for the different sampling stations, whereas Mn has a high concentration compared to the other stations, However the trace elements, with the exception of Khnifiss Lagoon (Morocco), are characterized in general by the lowest concentrations in our sampling site.

Table 3. Comparison of chemical composants in Oued Sebou with the sediments of other national and international rivers.

Elements	Fe	Mg	Mn	Zn	Cr	V	Pb	Cu	Co	As	References
concentrations	mg/g			µg/g							
Sebou, Kenitra (Morocco)	36	15	4	104	80	71	19	18	14	5	Our study
Bouregreg, Rabat (Morocco)	20	-	-	197	22	-	128	34	-	-	[12]
Loukkos (Morocco)	27	-	-	115	-	-	69	17	-	-	[12]
Bouregreg, Rabat (Morocco)	-	-	0.77	-	-	103	-	-	15	36	[13]
Sebou, fez (Morocco)	25	17	0.4	141	89	-	61	76	7.5	-	[14]
Fouarat lake, Kenitra (Morocco)	-	-	0.4	219	74	-	65	46	-	-	[15]
Moulay Bousselham Lagoon (Morocco)	45	-	0.33	210	47	-	28	55	-	-	[16]
Boumerzoug Basin (Algeria)	-	-	-	182	47	-	66	52	-	-	[17]
Rade de Toulon (France)	-	-	-	337	72	-	173	307	-	26	[1]
Khnifiss Lagoon, Tarfaya (Morocco)	-	-	-	52	27	39	6	7	4	9	[18]
Lake Łebsko, southern Baltic Sea (Poland)	-	-	-	-	29	-	31	43	-	-	[19]
Huixian wetland, Guangxi (China)	-	-	-	125	115	-	45	37	-	18	[20]

3.1.2. Discussions

Generally, Fe probably comes from agricultural activities. Indeed, Oued Sebou is characterized by the presence of important areas of agricultural activities. We can assume that the leaching of soils (especially at this period following the flooding) would be the major cause of the iron enrichment. Fe can also come from anthropogenic sources, in particular rail traffic, roads [21], air and sea traffic not far from the sampling sites. Mg can have a natural origin (mafic or ultramafic rocks or calcareous rocks) [22] or anthropogenic source (use of fertilizers) [23]. For Mn, we can say, like the case of Fe, that agricultural activities are responsible for Mn enrichment. Also, the natural origin can also contribute to the presence of Mn, since the formations of the watershed are rich in Mn (*limestone*, *marl*, ...) [2, 24]. Trace elements expressed in µg/g are probabely from auto-exhaust emission together with atmospheric deposition, especialy for Pb [25], domestic and industrial sources; such as sugar mills, paper mills, oil mills, tanneries, cement plants, the textile industry and the oil refinery [6, 26]. The levels close to the average value of the reference stations, suggest a natural contribution in connection with the geological nature of the terrain. While the results for Zn, Cr, V and Pb suggesting the involvement of human activities at the sampling sites.

3.2. Analyse en composantes principales

3.2.1. Results

To establish relationships between the chemical components and verify the similarity of its sources in the sediments of the Sebou Estuary, a correlation matrix has been realized on 11 elements and for 5 sampling sites. The interelemental correlation coefficients for five sampling sites are given in Table 4. Correlation matrices showed that there is a positive correlation of Cr and V with Fe and Cu on the one hand and with Mg on the other hand. We also have a negative correlation of Zn and Pb with Mn and Sr and positive correlation with As. In addition to a correlation between Pb and Cu.

Table 4. Interelemental correlation matrix for different sampling sites.

	Fe	Mg	Mn	Sr	Zn	Cr	V	Pb	Cu	Co	As
Fe	1										
Mg	0,37	1									
Mn	-0,35	0,35	1								
Sr	-0,47	0,61	**0,79**	1							
Zn	0,45	0,22	**-0,82**	-0,37	1						
Cr	**0,72**	**0,90**	0,22	0,27	0,22	1					
V	**0,84**	**0,75**	0,11	0,04	0,20	**0,96**	1				
Pb	0,67	0,24	**-0,82**	-0,51	**0,95**	0,36	0,41	1			
Cu	**0,96**	0,45	-0,39	-0,39	0,59	**0,72**	**0,78**	**0,75**	1		
Co	0,64	-0,22	-0,03	-0,58	-0,27	0,22	0,45	0,01	0,45	1	
As	0,55	0,42	-0,56	-0,25	**0,74**	0,48	0,54	**0,82**	0,53	-0,06	1

In order to confirm the correlations obtained, we applied Principal Component Analysis (PCA). The application of PCA allowed the extraction of three components with eigenvalues greater than 1 and a cumulative variance of 96.74%. The matrix of the components, after rotation of Varimax with Kaiser normalization, is given, for all the variables considered, by the Table 5.

We also introduced the quality of the representation of variables (extraction). The extraction values vary between 78% and 100%, hence the conclusion that all the variables studied are well represented and taken into consideration by the Principal Component Analysis. For each component obtained by PCA, we can define a correlation, characterized by a signature (elements contributing more than 50% to the source) and a counter-signature (elements presenting a zero correlation with the components of the PCA). A signature is defined by a grouping of the characteristic elements of the source [27]. We are interested here in the chemical components whose correlation is close to 1 (shown in bold in the Table 5).

Table 5. Matrix of Components after rotation as well as the quality of representation.

Element	Component			Extraction
	1	2	3	
Fe	**0.66**	0.42	**0.63**	1.00
Mg	**0.92**	0.04	-0.39	1.00
Mn	0.31	**-0.92**	-0.26	1.00
Sr	0.35	-0.53	**-0.77**	1.00
Zn	0.15	**0.97**	-0.10	0.97
Cr	**1.00**	0.08	0.05	1.00
V	**0.94**	0.11	0.29	0.99
Pb	0.28	**0.95**	0.15	1.00
Cu	**0.66**	0.51	0.47	0.92
Co	0.17	-0.19	**0.96**	0.99
As	0.43	**0.77**	-0.04	0.78
Eigen value	7.53	3.12	1.99	
% Total variance	50.29	28.35	18.10	
% Cumulative variance	50.29	78.64	96.74	

3.2.2. Discussions

The first component explains 50.29% of the variance of all data. It shows a good correlation between Mg, Cr and V and two less significant with Fe and Cu. This means that these elements vary in a similar way in the sampling sites. Indeed, the association between these major and trace elements can be interpreted by the selective absorption of Cr, V and Cu by sediments rich in Fe and Mg. It is therefore a source of various origins. In addition, For Fe and Cu where the correlations are less good, we can assume also the existence of local sources which bring fluctuations on the measurements and degrade the correlation coefficients, such as road, rail, air and sea traffic, not far from the sampling sites.

The second component, with 28.35% of the total variance, is strongly correlated with Zn, Pb and As. Mn is negatively correlated with these elements. That is to say, the behavior of the elements is done in the opposite way, if Mn increases, Zn, Pb and As decrease and vice versa. Indeed, because of the strong flooding in the area, trace elements (Zn, Pb and As), expressed in µg/g were transported by the suspended particles. While the observed anti-correlation for Mn may be due to the leaching of soil, near Oued Sebou, rich in Mn. especially since pollution or contamination by Mn is considerable ($3 \leq CFi < 6$) as seen before [10, 11].

The last component explains 18.10% of the information. It associated positively the Fe and the Co and negatively the Sr. In a similar way, we can say that the observed anti-correlation expressed by the sign (-) with Sr is explained by the different behavior of these elements compared to Fe and Co. In fact, we can assume that these three elements have a natural source, with an important concentration of Fe. The observed anti-correlation with Sr can be explined by the ability of these compounds to move quite easily because many of them are soluble especially after a period of flood. In addition, in a similar way to the first component, we can say that the less good correlations are due maybe to the existence of local sources which bring fluctuations on the measurements.

4. Conclusion

The objective of this study was to determine the origin of pollution and the impact of the flood period on the 11 chemical components considered in this work. For this, we have based on several data processing methods, namely, simple chemical characterization, calculation of contamination factors, comparison with quality standards or with similar works, the presentation of the correlation matrix and the application of the Principal Component Analysis. These different methods allowed us to clearly illustrate the natural (Fe, Mg, Mn, Co and Sr) and anthropogenic (Zn, Cr, V, Pb and Cu) origins in addition to the impact of the flood period on the evolution and variation of different chemical components. Especially for the Mn, which has high concentrations compared to similar works and whose contamination factors are considerable.

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Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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