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Spatial distribution and risk assessment of some heavy metal ions in the surface sediments of the lagoon of Nador.

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Abstract

Due to poor mixing and longer residence times in coastal lagoons, the impacts of anthropogenic activities are often more marked than in other coastal ecosystems. With a view to bring a contribution to the inventory of the spatial organization of metal pollution history in the surface sediments of the Nador lagoon, we conducted a comparative study on five heavy metals namely chromium, copper, iron, manganese and zinc in the superficial sediment covering 11 positions along the continental side of the lagoon. For this, we carried out two sampling campaigns: the first in November 2007 and the second in April 2008. The results were spatialized using geographic information system GIS in view to establish the relation between the levels of contamination observed for each species and their spatial distribution. According to the experimental conditions adopted in the present work, our results showed that the five metal ions can be detected in the range of mg/kg in the sediment samples with an acceptable confidence level. In these conditions, the most important levels were observed for iron and manganese which exhibit a variation with the sampling position indicating the impact of old iron mining near this area.

1. Introduction

Due to their important role as part of the geoenvironment, sediments are receiving much more attention from researchers and policy makers than it was in the past [1]. Sediments represent an essential resource in river basins and other aqueous environments as they contribute to the biodiversity for humans as construction materials, sand for beaches, and farmland and wetland nutrients. Unfortunately, the close contact with the water environment makes them both a source and a sink for contaminants due to some natural chemical and physical processes such as precipitation, hydrolysis and adsorption of a large amount of metals.

The Nador lagoon (34°54’N–02°10’W and 35°17’N–03°05’W) is the second lagoon complex of northern Africa [2] with an area of about 115 km^2. It is designated Ramsar site under N° 1484 since 2005. The major bordering locations are Beni Ensar city at northwest, the commune of Kariat Arekmane at the southeast and the northern extremity of the plain of Bou Areg at the southwest. This lagoon is protected by a particular thin sandy landform of about 25 Km long and 300 to 400 m width, which communicates with the Mediterranean Sea through an artificial inlet.

For many years, the Nador lagoon was submitted to several disturbances in connection with industrial development, intensive farming and many other sources of pollution. The Nador lagoon is one of the most interesting marine sites and nowadays a huge attention is being devoted for the rehabilitation through a vast development program. Several scientific national and international studies have been devoted especially to this Mediterranean lagoon [3-12] and most of them deal with important aspects such as environmental, geochemical, biological and simulation studies.

The Nador lagoon is fed by the marine waters entering via its natural pass, the water table of Bou Areg plain, and the waters from the different wadis and other temporary small watercourses. The main permanent wadis are:

- Wadi Bouaroug, whose mouth is located in the south of the city of Nador;
- Wadi Selouane, which represents the largest flow in the watershed;
- Wadi Afelioun, located at the southeast end of the lagoon.

These continental inputs have a direct impact on the nutrient concentration of the lagoon ecosystem as they get very concentrated and generally induce dystrophic crisis [13]. Among them, heavy metal ions which are well known for their toxicity and have been the subject of many studies regarding sediments and biota systems which proceed generally by bioaccumulation and magnification. Thus, they are considered as natural recorders of the metal pollution events.

Even though numerous studies have been devoted to this subject, concentration and distribution of heavy metals within the Nador lagoon with data pertaining to these last decades remain scarce, and in this context, it was necessary to quantify some heavy metals cations in the sediments in view to contribute to the assessment of the environmental quality in the period 2007-2008.

In order to bring a contribution to the spatial distribution of the metal pollution in Nador lagoon, we undertook a comparative study of the contamination of the sediment with five heavy metals ions : Cr(III, VI), Cu(II), Fe(II, III), Mn(II) and Zn(II) which major industrial uses have been compiled in previous studies [14, 15].

For this, we conducted two sampling campaigns of sediment in November 2007 and April 2008.This period is not covered since the latest literature does not report any paper referring to heavy metals contamination of the lagoon. The results were spatialized in order to bring a precise idea on the geographic repartition of the major metallic elements in the lagoon. Whenever possible, and regarding to their spatial repartition, relation between the different parameters in this survey is indicated.

2. Experimental

2.1. *Geographic situation*

Eleven sampling locations were chosen in order to bring a maximum information on the levels of the five metal ions in this area. Figure 1 shows the location of the lagoon in the entire map of Morocco and the precise locations of the sampling sites were measured using a GPS (E – map GARMIN) are gathered in Table 1.

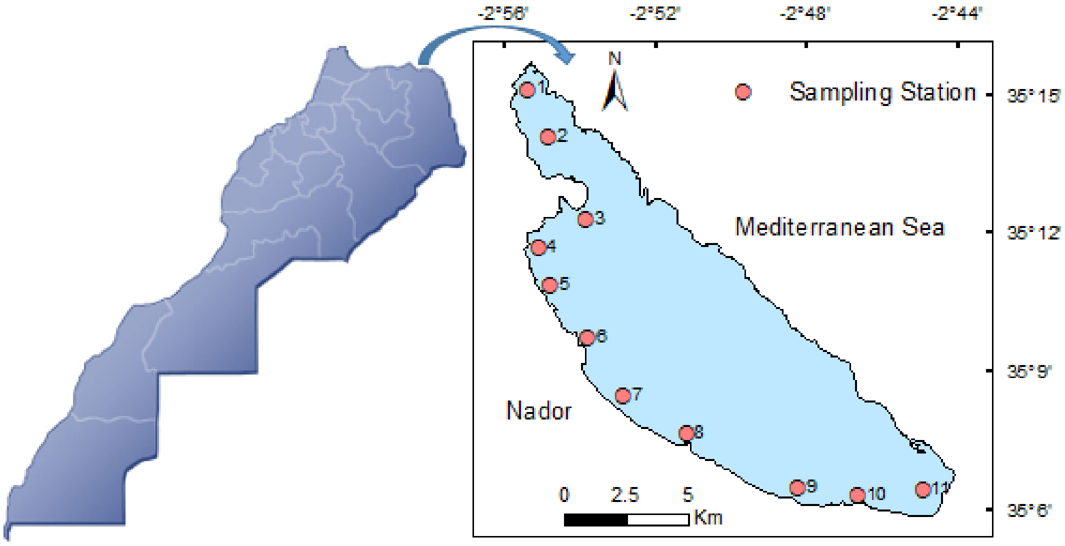

Figure 1: Map of Morocco and geographic situation of the sampling stations in the lagoon of Nador.

Table 1: Summary of the location geographic coordinates considered in this study.

Station	1	2	3	4	5	6	7	8	9	10	11
Long. W	2.92198	2.91374	2.89772	2.92107	2.91969	2.90413	2.88811	2.8579	2.81028	2.78135	2.75261
Lat. N	35.25355	35.23635	35.20578	35.19568	35.17959	35.16163	35.13992	35.12644	35.10585	35.1039	35.10547

2.2. *Samples collection*

It is very known that sampling of sediments, water or biota is a complex problem [16]. Therefore, experimental studies were carefully designed in order to evaluate the resulting data objectively.

Since the sediments present a natural variability, we paid a particular attention to the sampling method and closely followed the same protocol for the different sites. The literature is abundant and many sampling guidelines relative to this procedure are available [17, 18]. For each location, our diver used a long polyethylene tube as a corer to collect sediments. Since natural sediment formed during weathering processes may be modified quite markedly during transportation, only the 2 cm upper side of the core was removed and transferred under nitrogen flow in a high density polyethylene small container. The nature of the superficial sediments present in the lagoon is well described in a recent geological study [19]. All the samples were maintained at ca. 4 °C in a cool box and were carefully stored in a normal refrigerator at -18°C which is sufficient for the conservation since the analysis were carried out in the same week.

2.3. *Preparation of samples for analysis*

The analytical performance of our results was accredited through the participation of our Laboratory (Department of Chemistry) in several International Intercalibration Exercises coordinated by the International Atomic Energy Agency (IAEA) for heavy metals as we took part in the certification of some reference materials [20-22]. Therefore, we use the same protocol as recommended by the IAEA Marine Environmental Laboratory (Monaco) in their reported guidelines [17]. All samples were dried, made homogenate as described in the latter reports. Strong acid attacks using ultra-pure hydrochloric, nitric and fluorhydric acids in Teflon bombs. The optimization of the procedure took into account the recommendations of the literature [23, 24].

2.4. *Spectrophotometric analysis*

Flame Atomic Absorption Spectrophotometry FAAS was used for the analysis of total metal ions with the help of a Varian A20 double beam spectrophotometer equipped with a Varian hollow cathode and a Deuterium background corrector. Both standards and samples were acidified using Merck nitric acid and all samples to be analyzed were prepared in triplicate. All metal contents reported in this work refer to the initial dry mass. Mean metal concentrations are reported when their RSD do not exceed 5% which corresponds to the acceptable variability of the FAAS technique within the different replicates.

2.5. *Quality Assurance*

A certified reference material from IAEA was subjected to the same analytical procedures in order to evaluate the precision and accuracy of the method.

For each metal ion, the MDL (method detection limit) was determined using seven replicates with known concentration and the resulted standard deviation value was multiplied by the Student's t-value (3.143) for 99% confidence interval. The MQL (method quantification limit) was determined considering five times MDL, dilution factor, and the sediment weight sample. The wavelength, MDL, and MQL for each element are gathered in table 2.

Table 2: Wavelength, MDL and MQL for the different metal ions under investigation.

Element	**λ (nm)**	**MDL**	**MQL**
Cr	267.7	0.12	0.60
Cu	327.4	0.10	0.45
Fe	238.2	0.23	1.30
Mn	257.6	0.24	1.24
Zn	213.9	0.52	2.50

For the validation of the different analysis presented in the present work, we conducted a series of analysis on IAEA 158-TM which is a marine sediment certified reference material obtained from the IAEA Monaco during the participation of our laboratory in the Intercalibration exercise [22]. As shown in table 3 where concentrations were determined relative to dry-weight, our results are in good agreement with the reference sheet of this material.

Table 3: Elements considered in this study *vs* IAEA 158-TM marine sediment

IAEA-158 TM	**Certified values**	**This work mg/Kg**	**RSD**
Cr	74.4	78	3.8
Cu	48.3	43.4	3.5
Fe	26.3	24.8	4.4
Mn	356	348	4.6
Zn	140.6	147	4.8

3. Results and discussions

All analysis results need to be compared with references in order to give more interpretive results. As there is no universal guidelines for heavy metal intervals in marine sediment, and in general in aquatic environments, we chose to present our analysis using the criteria known as Sediments Quality Guidelines SQGs [25-28]. These latter are adopted in the Sediment Quality of the Canadian Ministry of the Environment [29] and meets largely those developed by Buchman [30] as a preliminary tool for screening purposes only for the US National Oceanic and Atmospheric Administration NOAA known as Screening Quick Reference Tables or SQuiRTs [31]. This SQGs recommended for Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Silver and Zinc tend to reflect any relationship between the concentrations of chemicals in sediments and any adverse biological effects arising from long contact with such chemicals. These latter are based on the chemical concentration in the sediment that causes an effect on aquatic species. Two reference values are established, the threshold effect level (TEL) which represents the lowest concentration below which adverse biological effects are expected to occur rarely and the probable effect level (PEL) which defines the level above which adverse effects are expected to occur frequently. More recently, three additional reference values were added, the rare effect concentration (REL) within which adverse effects are rarely observed, the occasional effect level (OEL) and the frequent effect level (FEL). These ranges were defined [32] assuming that the toxicity resulting from exposure to a chemical potentially increases with increasing concentration of the chemical in the sediment.

Table 4 gathers reference values as described above for Cr, Cu and Zn [33] to be compared with our results for these elements obtained in most cases with a relative standard deviation RSD less than 5% which is commonly accepted for AAS flame analysis. Their relative concentrations are discussed according to the above nomenclature and spatialized in the lagoon area.

Table 4: Concentrations in mg/Kg as classified and described in reference [33].

	REL	TEL	OEL	PEL	FEC
Cr	30	52	96	160	290
Cu	11	19	42	110	230
Zn	70	120	180	270	430

3.1. *Chromium*

The most known and stable oxidation states of chromium are III and VI. Trivalent chromium is naturally present in the environment and plays an important role in some biological processes, whereas Cr(VI) is mainly produced by industrial processes and is considered as a harmful substance due to its oxidizing potential. In estuarine conditions, the chromium behavior relies considerably on its valence [34, 35]. It is worth noting that AAS analysis used in this study refers to total concentration of chromium and the determination of the percentage of each species needs a more complicated technique.

Table 5 shows that for both campaigns, the concentrations never exceed the OEL level. As can be seen in figure 2 the highest concentrations were found at both ends of the lagoon (stations 10, 11) and at the adjacent part of the Bouareg plain. The highest values of the RSD confirm the heterogeneity of the repartition of this element (11-83 mg/Kg) which is in good agreement with a study previously carried out in the lagoon between 2000 and 2003 [6]. Furthermore, these concentrations can be considered typical for uncontaminated marine sediments as they are generally for sediment marine in the range of 50 to 100 mg/g dry weight [36].

Table 5: Total Cr concentrations for campaigns 1 and 2 (mg/Kg)

Station	1	2	3	4	5	6	7	8	9	10	11	**Mean**	**RSD**
Cr_1	53	12	21	41	18	11	29	52	52	22	58	**34**	53
Cr_2	48	61	47	75	36	39	53	44	59	77	83	**56**	28

3.2. *Copper*

All natural waters and sediments contain copper in its mono and divalent oxidation states and in several chemical forms. Copper plays vital roles as an essential plant nutrient and takes part to many metabolic activities of the organisms. However, it may become toxic to aquatic organisms in some specific conditions [37].

Results of table 6 represented in figure 3 show that particularly in station 6, and for a lesser extent in nearby station 5, copper concentrations are the most important and reaches 153 and 160 mg/Kg respectively for campaigns 1 and 2 in station 6. This value exceeds widely the Probable Effect Level of 110 mg/Kg.

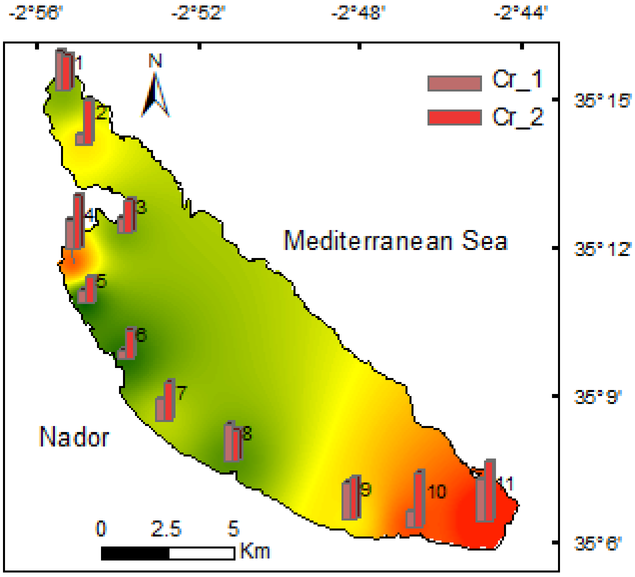

Figure 2: Spatialization of Cr in the Lagoon.

Table 6: Total copper concentration (mg/kg) for campaigns 1 and 2.

Station	1	2	3	4	5	6	7	8	9	10	11	**Mean**	**RSD**
Cu_1	31	54	49	29	69	160	12	23	21	25	22	**45**	93
Cu_2	2	17	27	27	61	153	5	7	11	14	6	**30**	148

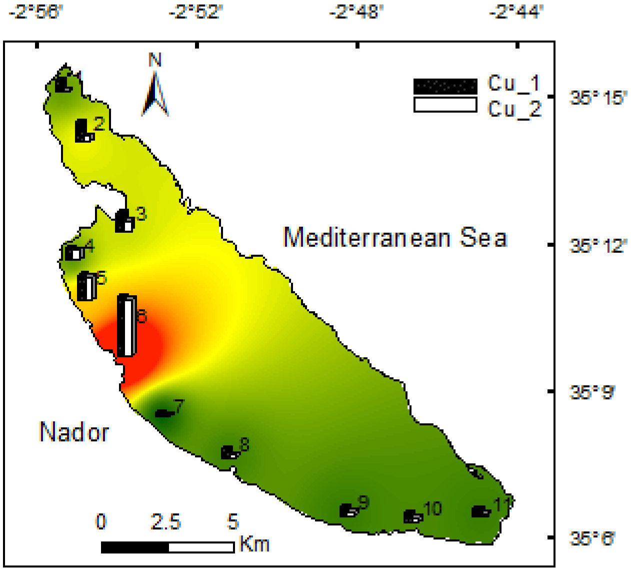

Figure 3: Spatialization of copper relative to campaigns 1 and 2.

Moreover, the mean values calculated separately for both campaigns remain in the interval of uncontaminated marine sediments 10-50 mg/Kg according to the literature [38, 39], but the higher RSD values show clearly how the repartition is heterogeneous. Indeed, stations 5 and 6 which face the Bouaroug wadi exhibit the higher concentrations which reflects the contribution of the urban agglomeration of Nador. The Sewage treatment plant being situated near the mouth of this wadi but not yet equipped at that time for the purification of such contaminants. The sediment of the remaining locations seems to be unimpacted by this metal ion.

3.3. *Manganese*

Manganese is an abundant constituent of the environment comprising about 0.1% of the earth's crust [40]. It's valence ranges from 0 to +7 with +2 as the most stable oxidizing sate. It is also known for its role in several enzymes in mammals [41] and as a micronutrient for marine organisms in photosynthetic and radical scavenging enzymes [42]. Manganese is not found in nature in its pure form but is present in more than 100 ores and minerals, including pyrolusite and rhodochrosite [43]. It is found in natural surface water and groundwater at various concentrations.

In some countries where Manganese is used in its organometallic Methylcyclopentadienyl Manganese Tricarbonyl MMT as an anti-knock additive in fuel [44], atmospheric traces of this element were expected to exceed 0.05 µg Mn/m^3 [45] which may contribute as an undesirable input in the marine environment.

Seawater contains around 0.4 to 10 µg /L [46] while drinking water is limited to 50-100 µg/L in most countries.

As shown in table 7 where data analysis are summarized for both campaigns, concentrations of Mn present two peaks for stations 6 and 3. This is illustrated in figure 4 where we can easily see that station 6 is the most exposed to anthropogenic and natural inputs as it is situated in front of the mouth of the Bouaroug wadi which drains untreated sewage water of Nador city. Knowing that Manganese is usually found in combination with iron, values observed in station 3 are in agreement with the fact that the geographic situation is very close to the peninsula of Atalayoun where iron mine dumps were stored in the seventies and eighteens.

Table 7: Total manganese concentration (mg/kg) for campaigns 1 and 2.

Station	1	2	3	4	5	6	7	8	9	10	11	**Mean**	**RSD**
Mn_1	138	283	614	332	343	614	385	273	270	325	298	**352**	41
Mn_2	46	150	494	260	339	629	224	196	185	380	106	**274**	63

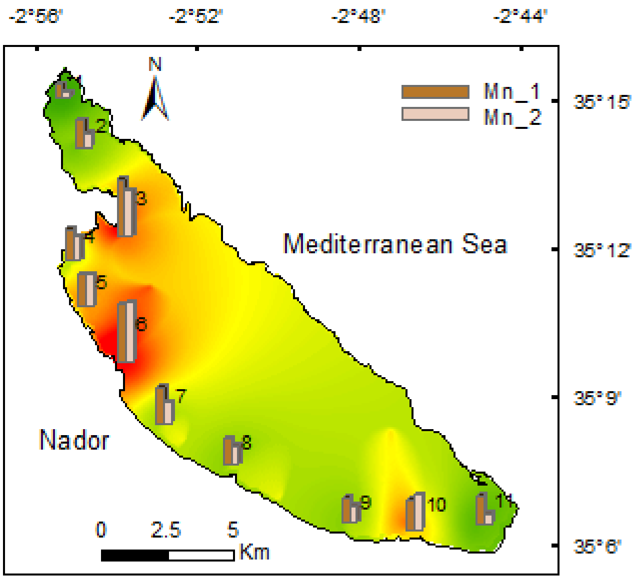

Figure 4: Spatialization of manganese relative to campaigns 1 and 2.

The discharge of leachate coming from this mining heaps contribute to the enrichment of this area by several heavy metals.

The southeast stations 10 and 11 are located near the agglomeration of Arekmane and present relatively higher concentrations of Mn and reflects all the forms of the man-made inputs as all the sewage water were drained at that time directly in the lagoon without any purification.

To our knowledge, there is no data referring to normal concentration values of this element in marine sediments. Nevertheless, our results, when compared in terms of their means, are in good agreement with those conducted in 19 UK sediments estuaries with concentration of Manganese varying from 241 to 1169 mg/Kg [47].

3.4. *Iron*

Iron is the most abundant in the Earth overall and fourth most abundant element in the crust (5%). It is also the most abundant transition element and is probably the most well-known metal in biological systems. However, this abundance does not correlate to its dissolved Fe concentrations in open-ocean seawater as it is in the level of subnanomolar [48].

This element is present under several forms in the marine sedimentary systems and is delivered by riverine transport, airborne dust and from submarine volcanic exhalations. Due to the oxic nature of the seawater, iron accumulates in sea floor sediments in the dominating ferric Fe^{+3} form [49] and its redox properties in aquatic medium play an important role in the natural cycling of carbon, sulfur, phosphorus, and several trace elements [50].

One should allow a particular attention to this element since as it is mentioned above, iron mining was very active in the beginning of the last century and closed earlier in the 80's. It is situated in the district of Ouiksane some 15 Km at the southwest of the lagoon. The literature relative to Fe analysis in marine sediments are very abundant. Unfortunately, there is no reference guidelines for this element and comparison with other studies targeting surface marine sediment may help to the situation of the lagoon. For comparison reasons, table 8 gathers maximum concentration in mg/Kg of iron observed for some selected areas in the world.

Table 8: Comparison of Fe concentration in superficial sediments (mg/kg) in other marine sediments studies in the world.

Site	Country	Fe (mg/Kg)	Ref.
Quintero bay	Chile	94341	[51]
Lagoon of Nador	Morocco	76429	This work
Santos-São Vicente Estuary	Brazil	43798	[52]
Jiaozhou Bay	China	29400	[53]
25 de Mayo Island	Antarctic	19665	[54]

25 de Mayo or King Georges Island, one of the last unspoiled areas in the planet, is situated in the Antarctica and is practically always cited in marine environmental studies to justify to some extent the anthropogenic contribution from the other sources.

Sedimentary Fe in the Jiaozhou bay is ascribed by the authors to natural weathering sources, without appreciable anthropogenic inputs whereas the industrial activities (copper smelter and thermoelectric power) are considered to be at the origin of the high level of Fe in the Quintero Bay for which this assumption was corroborated using an uncontaminated reference site as control point at a depth of 19 meters (Fe: 26620 mg/Kg).

The concentration of iron as recorded in the Nador Lagoon depends extremely on the position of the sampling site. Sediments have ranged between 17579 and 76429 mg/Kg for campaign 1 and between 13843 and 67143 mg/Kg for campaign 2 with very close averages and the same RSD values (see table 9). The spatialization of the whole data illustrated in figure 5 shows clearly that stations 5 and 6 which face the city of Nador are the most contaminated with a maximum value of 76429 in campaign 1. This result is unfortunately comparable to those observed in the Santos São Vicente estuarine system which is situated in an Industrial Complex and show a high value of Fe concentrations [52].

Table 9: Total iron concentration (mg/kg) for campaigns 1 and 2.

Station	1	2	3	4	5	6	7	8	9	10	11	**Mean**	**RSD**
Fe_1	42919	20521	28450	32757	40769	76429	17579	29462	25643	25986	28193	**33519**	48
Fe_2	32907	13843	23950	34579	50714	67143	23643	26293	20350	25593	25523	**31322**	48

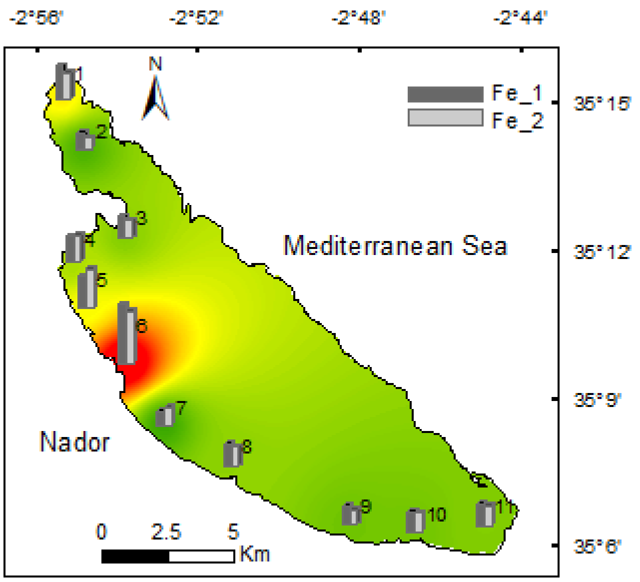

Figure 5: Spatialization of iron relative to campaigns 1 and 2.

The station 1 exhibits a relatively higher concentration as it is in the vicinity of Beni Ansar agglomeration. The situation in station 3 near Atalayoun peninsula where mining heaps were stored during the iron mining activities in the region is a good surprise since the levels observed are practically identical to some reference values and may be designated as a background Fe level. On the other hand, all the other stations around the lagoon exhibit moderate levels of Fe and can be regarded as a very similar to those reported for natural concentrations.

3.5. *Zinc*

Zinc is the 24th most abundant on Earth with only about 0.007% of the Earth's crust [43]. It is used in alloys since the Babylonians over 5000 years ago. In aqueous solutions, the most stable form of Zn is the free ion Zn^{2+} and it is often the most abundant of the dissolved forms of Zn.

It is known for its various applications in industrial and ornamental purposes including bronze and brass. Its role in enzymatic reactions is well documented as it participates to many vital biological processes [55].

Concentrations of Zn in seawater are less than 1 µg/L [56], but levels in coastal areas and estuaries are often much higher. In addition, zinc is not considered as being especially toxic to biota and vegetation mainly when it is in background levels, however excessive soils contamination from diverse sources has highlighted its phytotoxicity [57, 58].

Our results for Zn levels are reported in table 10 and spatialized in figure 6. The concentrations vary between 23 and 109 mg/Kg and were determined only during the first campaign with an average value of 73 mg/Kg and a less high RSD than the other metals.

Table 10: Total zinc concentration (mg/kg) for campaigns 1.

Station	1	2	3	4	5	6	7	8	9	10	11	**Mean**	**RSD**
Zn_1	60	23	82	109	107	86	81	64	90	23	84	**73**	39

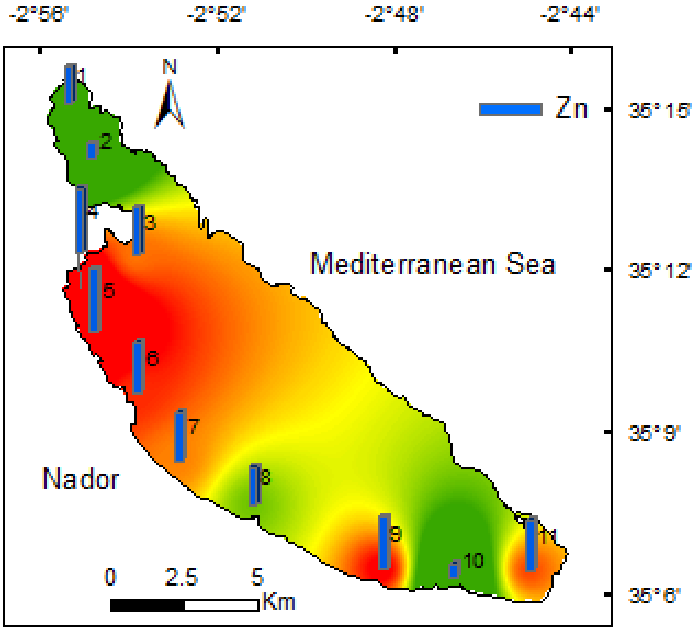

Figure 6: Spatialization of Zn in the lagoon for campaign 1

The first remark we can make is that all the stations around the lagoon exhibit concentration lower than the TEL as defined by the SQGs. The mean observed 73 mg/Kg is very close to the REL which confirms that this metal does not present any severe harmful effect. In addition and to our knowledge, there is only one published study during which this metal was analyzed [6] in surficial sediment between 2000 and 2003 in the same area with a mean value of 98 mg/Kg. This downward trend of about 25% must be confirmed and updated for the present day. The higher concentrations of Zn were obtained in stations 4 and 5 followed by the nearby ones such as 3, 4, 6 and 7 situated in the front of the Nador city confirms the anthropogenic contribution. Station 9 also exhibits a higher level and may reflect the diverse input coming from the different wadis. As for station 11, it's relatively high concentration of 84 mg/Kg may be ascribed to the anthropogenic and natural inputs.

Conclusion

This study was carried out on superficial sediment taken from eleven stations, which cover the entire continental border of the lagoon of Nador in order to evaluate the concentration levels of Copper, Chromium, Iron, Manganese and Zinc ions in this area taking into account quality assurance procedures. These results seem to be of great importance considering the lack of data covering the monitoring of different sources of pollution in this lagoon.

The levels of these selected metal ions were assessed throughout two campaigns carried out during November 2007 and April 2008. Unlike the other metal ions, iron exhibits a specific spatial distribution with a very high levels observed in the stations facing the old mining heap of Atalayoun peninsula and the agglomeration of the Nador city reflecting both inputs from old mining and anthropogenic activities.

When compared to some similar ecosystems in the world, it appears that, except for total iron ions, all the other elements are not in an alarming situation according to the SQGs. This fact was verified for some sites since the levels observed are practically in their background line.

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