Analysis of Heavy Metals in Sediments from Northern Moroccan Coast Using Simple and Low-Cost Methodology

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Abstract: A new simple and low-cost digestion method for sediment samples was studied and optimized. It was based on the acid digestions of samples into low-pressure PTFE bombs and heating in a simple convection-based oven, as an alternative to available standard methods based on high-pressure bombs and microwave ovens. Although there is no doubt about the benefits of microwave-based methodologies, there is still a problem related with the high cost of the equipment required, making difficult its practical application in some developing countries. The proposed methodology was optimized by using three certified reference materials (CRMs): marine sediment (GBW07313), estuarine sediment (SRM1646a) and river sediment (CRM320), which were digested separately by the two studied methods. Metal concentrations in the digested extracts were analyzed and compared. Average metals recoveries obtained with the new method ranged from 61 % (Al) to 100 % (Cd, Co, Pb), and, in general, significant differences between the two methodologies were not observed.

The new digestion method was applied to the simultaneous determination of up to ten heavy metals in marine sediments from the Northern Moroccan coastline, in the Mediterranean province of Tetouan and Chefchaouen. The results obtained ranged from 1.26-3.32 % for Al, 16.2-20.7 mg/kg for Co, 49.7-72.7 mg/kg for Cr, 20.2-32.3 mg/kg for Cu, 2.98-3.92 % for Fe, 184-394 for Mn, 34.5-44.3 mg/kg for Ni, 36.0-49.7 mg/kg for Pb, 0.46-0.55 % for Ti, and 67.5-83.6 mg/kg for Zn.

A statistical data analysis was performed in order to determine the sources of heavy metals in this area. Relatively high concentrations of Cr, Ni and Pb were measured in all the sampling sites, although their anthropogenic origin could not be established. In addition, Cu and organic matter were enriched in sediments close to agricultural areas.

Keywords: Sediments, heavy metals, anthropogenic pollution, acid digestion, Moroccan coast.

1. INTRODUCTION

Morocco, with more than 3500 km of coastline, finds in the marine environment one of the main basis of its economy, with fishing and tourism being the most prominent activities undertaken. For this reason, an effort is being made to establish and preserve the environmental quality of littoral zones, including the levels of different pollutants in Moroccan coast. These studies allowed the identification of contamination sources and the establishment of control measures if necessary [1-3].

In this context, the knowledge of heavy metals distribution in aquatic environments is of main interest due to their potential harmful effects on aquatic organisms, even at very low concentration, and they can be related with differ-

ent anthropogenic activities. Besides, aquatic sediments can play an important role as a trap of metallic elements. These metals may present both natural and anthropogenic origin [4], and then, they can be used as tracers of different anthropogenic activities [5, 6]. In this sense, high concentrations of Zn, Cu and Pb in marine sediments have been related to industry, urban settlements or aquaculture activities [7, 8].

Although several methodologies may be used to analyze metals in aquatic sediments, most of them are based on a previous sample digestion before metal quantification by different analytical techniques. The objective of the digestion step is to achieve a selective or complete extraction of metals from the sediment, while sample contamination is prevented. Mostly, the digestion procedures are based on the addition of inorganic acids in a closed vessel, which may be heated with different sources. For instance, aqua regia, HNO_3-HF, HF-HNO_3-H_2SO_4-$HClO_4$, HNO_3-$HClO_4$ has been proved to extract metals from sediments with variable effectiveness, and the addition of HF is always required to dissolve the

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silica matrix if a complete digestion is needed [9-12]. In addition to the acid mixture used, the selection of the heating source has been also reported to have strong influence in the digestion efficiency. In this sense, the use of microwave-assisted digestion is much extended, since it presents several advantages such as the use of small acid volumes, the reduction of the extraction time and the prevention of a possible loss of volatile elements caused by warming up the sample [10, 13]. Nevertheless, the main drawback of micro-wave systems is the high cost of the equipment required (both the oven and the bombs) that may be up to 50-100 times higher than convection ovens. This fact is very important especially in developing countries where the microwave systems are usually not available. For this reason, the development and optimization of less expensive diges-tion methodologies are also required.

In this work, a digestion method based on low-pressure PTFE bombs and a simple and low-cost convection-oven has been optimized and applied to the analysis of metals in marine sediments of the Morocco's Mediterranean coast.

2. MATERIALS AND METHODS

2.1. Study Area and Sampling

Two sampling areas were selected in the Morocco's Mediterranean Coast, in the Province of Tetouan and Chefchaouen (Fig. **1**). The first one was close to the urban area of Martil, and it receives the urban discharges from Martil city and Tetouan district. This zone is characterized by an important industrial and tourist activity, particularly in summer. The second sampling area, namely Oued Laou, is relatively far away from any urban area, although in this area is located the mouth of the Oued Laou River, which receives agricultural and untreated urban discharges.

The sediments analyzed were taken in October 2007. Sampling was carried out in four different sites in each sampling area following a transect perpendicular to the shoreline. A detailed description of each sampling point is presented in Table **1**. In each sampling site superficial sediments (5 cm depth) were taken in duplicate by using a Van Veen grab (305mm x 305mm), and avoiding sediment
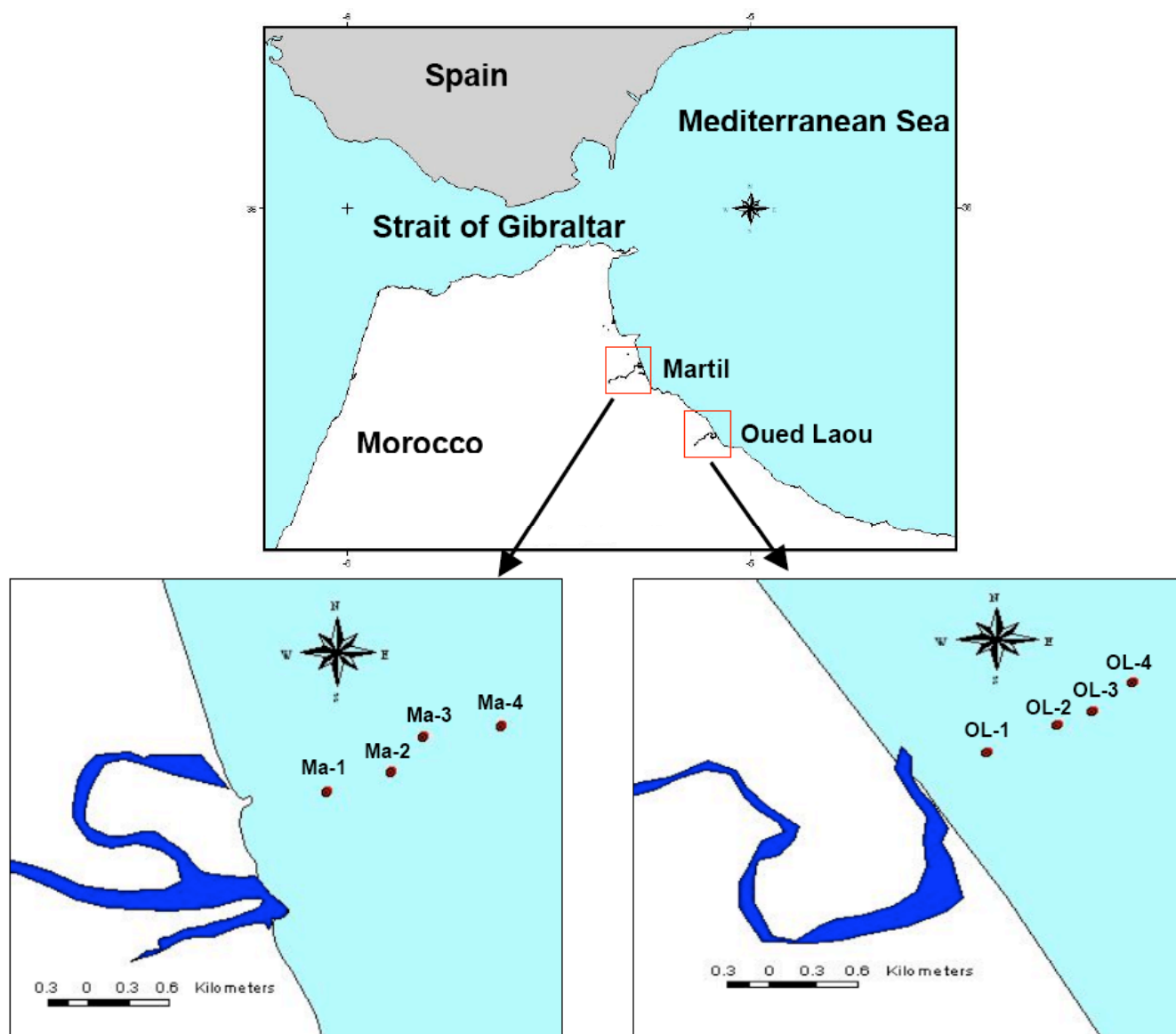

Fig. (1). Sampling stations of sediment in the Northern Moroccan coast.

Table 1.   Description of the Sampling Stations in Mediterranean Moroccan Coast

Sampling Location	Sampling Station	Latitude	Longitude	Depth (m)	Distance to the coastline (m)
Martil	P1	N35º36.540	W05º15.686	5	490
	P2	N35º36.625	W05º15.425	10	884
	P3	N35º36.770	W05º15.294	15	1185
	P4	N35º36.810	W05º14.976	20	1679
Oued Laou	P1	N35º26.147	W05º04.628	5	280
	P2	N35º26.272	W05º04.370	10	720
	P3	N35º26.331	W05º04.237	15	1010
	P4	N35º26.465	W05º04090	25	1300

loss as far as possible. Analytical procedures were performed with <63μm fraction, previously separated by wet sieving, dried at 105ºC until constant weight, and crushed before acid digestion.

2.2. Reagents and Solutions

All the acids used were of analytical reagent grade. Nitric acid (65% w/v), hydrofluoric acid (40% w/v), sulphuric acid (98% w/v), and hydrochloric acid (35% w/v) were obtained from Scharlab (Spain). Potassium dichromate, ammonium iron (II) sulphate hexahydrate and ferroin (0.025 M solution) were also purchased from Scharlab (Spain). Aqueous standards solutions of metals (Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, and Zn) were prepared from 1,000 mg L^{-1} standard solutions obtained from Merck (Germany). All solutions were prepared with deionized water (18 MΩ·cm^{-1}) from a Milli-Q analytical reagent grade water purification system (Millipore, Bedford, MA).

Three CRMs, were used to optimize the digestion method. The first one was marine sediment (GBW 07313), purchased from the National Research Center for Certified Reference Materials (China). The second was estuarine sediment (SRM1646a) prepared by the National Institute of Standards and Technology (USA) and the third one was river sediment (CRM320) supplied by the European Community Bureau of Reference (Belgium).

2.3. Apparatus

A microwave oven Ethos (Milestone, Italy) with temperature control and a convection oven P-Selecta (Selecta, Spain) were used to perform the digestion of the sediment samples. After the digestion step, the extracted metals were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES) IRIS Intrepid (Thermo Elemental, United Kingdom).

When the convection oven was used, samples digestions were carried out by using PTFE chemically inert bottles (Brand, USA). Before each digestion, they were soaked overnight into a mixture of HNO$_3$ and HCl (5:2).

2.4. Digestion Procedures

The metals analyzed in the sediments were Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, and Zn. To optimize the analytical method, the three CRMs mentioned before were digested by using both microwave and convection heating procedures. EPA method 3052 was adapted to reduce the amount of sample and consequently the volume of acids [14]. Thus, 0.2 g of dry sediment (<63μm) was placed in each microwave PTFE vessel and 1 mL HF plus 4 mL HNO$_3$ were added. The microwave heating program consisted of two steps. First, the temperature was slowly increased up to 180 ºC during 5 min and then, microwave radiation was used to maintain a constant temperature of 180 ºC for 15 min. Once PTFE bombs cooled down, the extracts were filtered, if required, and transferred into 50-mL volumetric flasks. Finally, the solutions were kept in acid-cleaned polyethylene bottles at 4 ºC until their analysis.

The convection-based procedure was identical, but substituting the microwave oven by a convection oven, and heating the samples at 105 ºC for 24 hours. The results obtained with both methods were statistically compared to confirm the applicability of the convection-based methodology to the analysis of real samples collected in the Moroccan coast.

2.5. Analysis of Organic Matter

To analyze the concentration of organic matter in the samples, 0.2 g of sediment were taken and oxidized for 30 min with 10 mL of K$_2$Cr$_2$O$_7$ 0.083 M plus 10 mL of H$_2$SO$_4$. Then, the excess K$_2$Cr$_2$O$_7$ was measured by back-titration with Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O and ferroine as indicator. A blank titration was carried out for each determination [15].

2.6. Statistical Procedures

The concentrations obtained in the analyses of the CRMs by both digestion methodologies were compared by using the Student's t-test [16] and, on the other hand, metal recoveries were compared using ANOVA or Kruskal-Wallis tests. Finally, for data interpretation, the concentrations of

Table 2.   Total Metal Concentrations in Three Certified Sediments Obtained by Using Digestion Procedures Based on Microwave and Convection Ovens

Sample		Al (%)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (%)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Ti (%)	Zn (mg/kg)
GBW 07313	Certified	-	76.6 ± 3.2	58.4 ± 3	424 ± 19	-	-	150 ± 8	29.3 ± 2.4	-	160 ± 6
	Microwave	6.4 ± 0.2	78.2 ± 4.4	43.7 ± 3.0	401.2 ± 27.5	4.0 ± 0.1	3171.4±212.7	159.2± 14.4	24.0 ± 2.8	0.4 ± 0.1	107.7 ± 5.1
	Convection	5.6 ± 0.1	62.2 ± 10.5	44.9 ± 6.6	398.7 ± 10.0	4.0 ± 0.1	2273 ± 548.1	133.1 ± 6.6	32.9 ± 6.5	0.3 ± 0.1	143.9 ± 6.9
SRM1646a	Certified	2.3 ± 0.1	5*	40.9 ± 0.9	10.0 ± 0.1	2.0 ± 0.1	234.5 ± 1.4	23*	11.7 ± 0.6	0.5 ± 0.1	48.9 ± 0.8
	Microwave	1.8± 0.5	5.0 ± 0.8	27.3 ± 1.5	7.0 ± 0.6	1.9 ± 0.1	242.7 ± 15.9	21.8 ± 0.8	14.6 ± 3.3	0.4 ± 0.1	33.0 ± 0.5
	Convection	1.5 ± 0.6	6.5 ± 1.7	25.7 ± 3.3	7.9 ± 1.6	1.8 ± 0.1	175.1 ± 22.0	16.7 ± 0.7	10.6 ± 3.2	0.4 ± 0.1	38.0 ± 1.8
CRM320	Certified	7.9 ± 0.5 *	19.4 ± 1.5	138.0 ± 3.5	44.1 ± 0.5	4.5 ± 0.2	740.2 ± 62.5*	75.2 ± 2.8	42.3 ± 1.6	0.5 ± 0.1*	142.0 ± 6
	Microwave	5.1 ± 0.9	23.2 ± 1.2	89.6 ± 5.2	44.2 ± 12.4	3.8 ± 0.1	760.8± 52.2	78.6 ± 5.6	43.4 ± 2.8	0.5 ± 0.1	93.8± 5.2
	Convection	3.0 ± 1.4	19.9 ± 1.9	82.7 ± 8.1	35.7 ± 8.9	3.5 ± 0.2	435.9 ± 67.6	66.5 ± 5.6	43.1± 5.0	0.5 ± 0.1	107.1 ± 7.1

(*) not certified

heavy metals in the sediments from north Moroccan coast were analyzed by principal components analysis (PCA). All statistics were performed using the SPSS15 software (http://www.spss.com).

3. RESULTS AND DISCUSSION

3.1. Digestion Procedures

The results obtained for the analysis of three CRMs by the new method (convection-based) and the reference method (microwave-based) are reported in Table **2**. As observed, some elements such as Al, Cr, Cu or Mn presented non-quantitative recoveries by both methods. For this reason, the use of a higher volume of hydrofluoric acid (2 mL) was tested in order to improve the recoveries without success. Similar results were reported by several authors for Al, Cr or Cu [17,18].

As suggested by the results of the Student's t-test presented in Table **3**, the results obtained by both methods were, in general, very similar. Null hypothesis was always accepted except for Al and Zn in the marine sediment. This

fact could be related with the observed partial solution of few refractory sample matrix compounds, such as alumina, and other oxides [14].

Average recoveries were calculated for each metal. With this aim, we took into consideration up to three recovery values, corresponding to the three CRMs analyzed by using the proposed convection method. To compare these values, Student's t-test was used if only two values were available, while ANOVA or Kruskal-Wallis test were used to compare the three values at a time. Final recovery values were estimated from marine sediment plus, if no significant different observed, estuarine and/or river sediment. The values obtained, and used to calculate metal concentrations in Moroccan sediments, were: Al (61 %), Fe (93 %), Ti (92 %), Mn (75 %), Co (100 %), Cr (76 %), Cu (86 %), Ni (95 %), Pb (100 %), and Zn (90 %).

3.2. Distribution of Heavy Metals and Organic Matter in Marine Sediments of the Moroccan Coast

The results obtained for the two sampling locations studied (Martil and Oued Laou) are presented in Figs. (**2-4**), for major and minor heavy metals, and organic matter,

Table 3.   Comparison between the Concentrations Obtained by the Two Heating Methodologies Using Student's t-Test

	GBW07313				SRM 1646a				CRM320			
	t_{exp}	t_c	d.f.[a]	H_0[b]	t_{exp}	t_c	d.f.[a]	H_0[b]	t_{exp}	t_c	d.f.[a]	H_0[b]
Al	5.38	3.18	3	rejected	0.69	2.45	6	accepted	2.19	2.57	5	accepted
Co	1.97	2.77	4	accepted	1.40	2.78	4	accepted	3.15	2.57	5	rejected
Cr	0.23	2.57	5	accepted	0.78	2.36	7	accepted	1.32	2.36	7	accepted
Cu	0.10	2.77	4	accepted	0.79	2.57	5	accepted	1.21	2.36	7	accepted
Fe	0.27	3.18	3	accepted	0.31	2.57	5	accepted	2.14	2.57	5	accepted
Mn	2.15	2.57	5	accepted	4.68	2.36	7	rejected	4.92	2.36	7	rejected
Ni	1.94	2.77	4	accepted	5.68	2.45	6	rejected	1.76	2.57	5	accepted
Pb	1.64	2.57	5	accepted	1.49	2.57	5	accepted	0.06	2.78	4	accepted
Ti	1.52	2.57	5	accepted	1.61	2.36	7	accepted	0.32	2.57	5	accepted
Zn	5.88	3.18	3	rejected	4.56	2.57	5	rejected	1.90	2.57	5	accepted

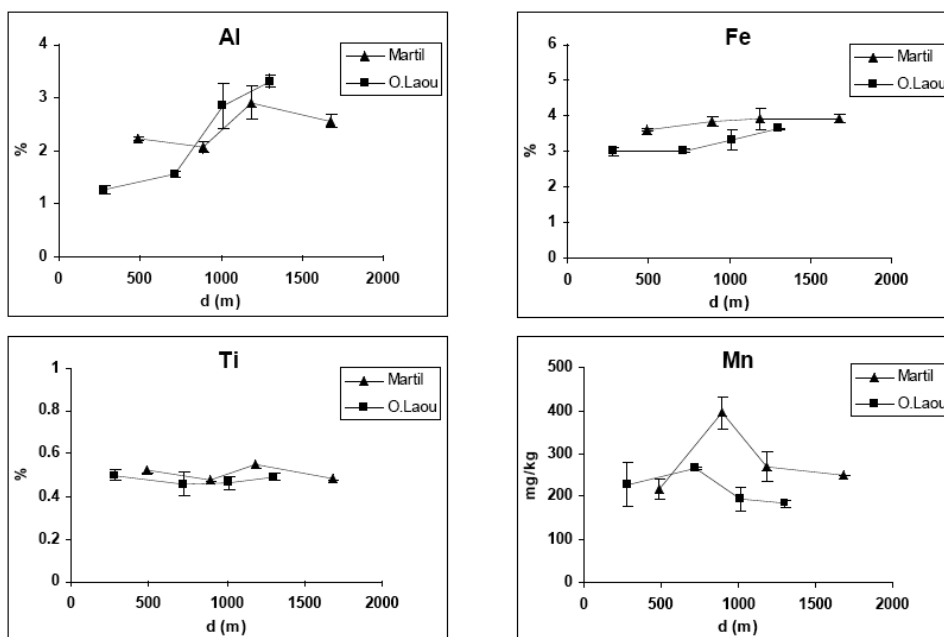(a) d.f.: degrees of freedom [15]; (b) H_0: Both heating methods give the same result.

Fig. (2). Concentrations (% dry sediment) of Al, Fe, Ti and (mg/kg dry sediment) of Mn in coastal sediments from Martil (▲) and Oued Laou (■).
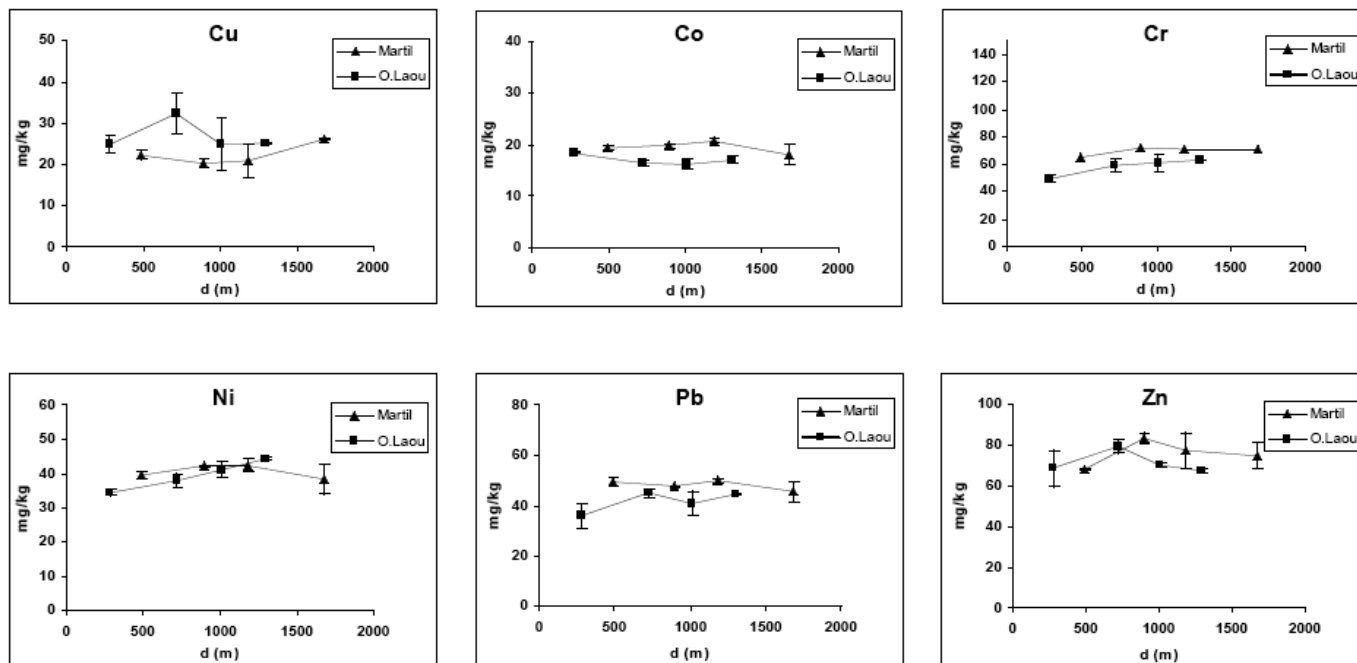

Fig. (3). Concentrations of Cu, Co, Cr, Ni, Pb, and Zn in mg/kg dry sediment in coastal sediments from Martil (▲) and Oued Laou (■).

respectively. In both sampling areas the concentrations of metals in the sediments were almost invariable with distance to the coast. This fact could be related with the presence of rivers mouths in both zones which could contribute to the homogenization of the sediments even at large distances from the coast. Nevertheless slight deviations from this general trend were observed for some elements. Thus, while Al increased its concentration with distance from the coast, Mn exhibited their highest concentrations in Martil in the second sampling station, about 700-900 meters away from the coastline. Since no pollution effect could be established

in this location, this higher concentration could be likely due to natural reasons, although this fact could not be established.

The concentrations of metals measured in Martil were in general higher than those measured in Oued Laou. The only exception was obtained for copper, suggesting a specific input of this element in the zone of Oued Laou. This input could be also responsible of the higher contents of organic matter measured in this zone, and it could be probably related with agriculture which is the main anthropogenic
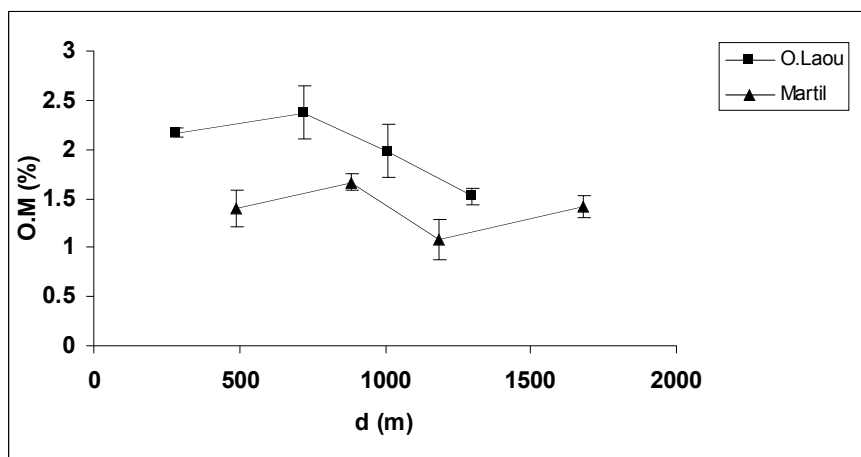
Fig. (4). Concentrations (%) of organic matter in coastal sediments from Martil (▲) and Oued Laou (■).

activity in the area. High copper concentrations in sediments have been previously related to agricultural activities in other zones [19].

If compared with the values reported by the most frequently used Sediment Quality Guidelines (SQGs), such as those developed by the Canadian environmental authority (Environment Canada) [20] and the American National Oceanic and Atmospheric Administration (NOAA) [21], the concentrations of Cr, Pb and Ni were above the recommended quality values, although they did not exceed the values causing probable effects in the organisms. On the other hand, if compared with a more local SQG developed for the Gulf of Cádiz (close to the Strait of Gibraltar), our results indicate a moderate pollution by Cu, Ni, and Pb, and a high pollution by Co [22].

3.3 Statistical Analysis

Multivariate analysis by principal components analysis (PCA) with standardized data was used for a better interpretation of the results obtained in the sediments of the Moroccan coast. Three principal components with eigenvalues higher than 1 were extracted, explaining 88.7 % of the variance of the system. As reported in Table **4**, the first one

Table 4.   Factor Loadings for Metal Concentrations in the Sediments

	PC1	PC2	PC3
Al	0.517	**-0.761**	0.351
Co	**0.747**	0.262	-0.609
Cr	**0.919**	0.065	0.300
Cu	**-0.731**	0.117	0.446
Fe	**0.927**	-0.140	0.089
Mn	0.499	**0.828**	0.100
Ni	0.659	-0.453	0.450
Pb	**0.837**	0.043	0.139
Ti	0.514	-0.278	**-0.736**
Zn	0.440	**0.785**	0.355

explained most of the variation of most minor elements, such as Co, Cr, Cu, and Pb, as well as Fe, indicating a similar source for these elements probably related to anthropogenic activities. Besides, only copper presented a negative load indicating a probably different anthropogenic source for this element in comparison with the others. The 2nd and 3rd PCs explained the major source of variation for most major elements, such as Al, Zn, and Mn, in the second, and Ti in the third one, being related to natural sources. Ni was distributed between the three components indicating a mixed (natural and anthropogenic) origin in the studied area.

To establish the sources of metals in the area, scores of sampling sites and loadings of variables are represented in Fig. (**5**), for the first two PCs. As can be observed, sampling stations corresponding to Martil and Oued Laou are clearly separated by the signal of the first PC. Besides, as mentioned before, Cu is the unique variable that presents higher concentrations in Oued Laou, and it is now separated from the rest of the variables, confirming its different origin, probably associated to agriculture as it was explained before.

The other metals appeared all together, and close to Martil sampling stations, suggesting a high homogeneity in the composition of the sediments of the area. Nevertheless three different metals subgroups could be separated. The first group included some elements that appeared at high concentrations in the samples, such as Co, Pb, Cr and Fe, and they could be related to the anthropogenic activities developed in Martil area, mainly urban and industrial activities. Similar association between Fe and Cr has been observed in sediments from rivers located in the Tangier area related to industrial activities, although in that case Ni and Cu were also related to industrial and urban sources [23]. The second group included the lithogenic elements Ti and Al, as well as Ni, suggesting that the high concentrations of this metal measured in the samples could not be clearly related to anthropogenic pollution. In this sense, high natural concentrations of Ni in crust have been previously described [24]. The third subgroup included Mn and Zn and, in this case, its origin appears related to natural sources, although the presence of anthropogenic Zn has been reported in other studies dealing with the Moroccan coastal sediments [25, 26].
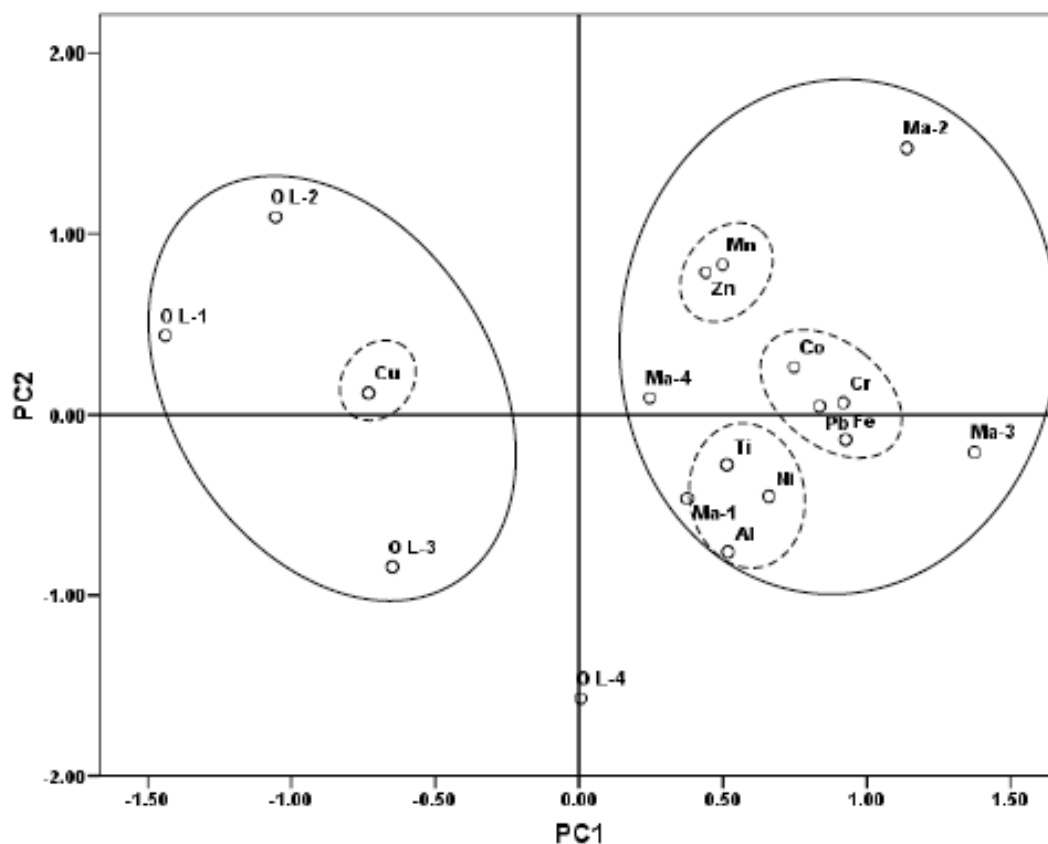
Fig. (5). Principal component analysis (PCA) for Al, Fe, Ti, Mn, Cu, Co, Cr, Ni, Pb and Zn in sediment collected from the Northern Morocco coast.

4. CONCLUSIONS

The results obtained for the determination of heavy metals in aquatic sediments by means of an acidic digestion of the samples in low pressure PTFE bombs and convection heating were significatively equal to those obtained by the more sophisticated and expensive methodology based on microwave ovens. The new methodology was applied to the analysis of metals in sediments from two different areas of the Mediterranean coast of Morocco. The results obtained suggested that, in general, metal concentrations were very similar in both studied areas, and presented low variability with distance to the coast, indicating high homogeneity in the sediments, probably caused by the presence of river mouths. Data analysis by PCA classified metals in three different groups: on the one hand, Co, Cr, Pb, and Fe, which appeared at high concentrations probably due to anthropogenic activities; on the other hand, Al, Ti, Mn, Zn, and Ni, which are likely to have a natural origin (probably mixed with anthropic in the case of Ni); finally, Cu presented a different and particular behavior, and was the only metal with lower concentrations in Martil than in Oued Laou, an area where agriculture activities are quite developed. Regardless of their origin, the results obtained reported high concentrations of several metals, such as Co, Cr, Ni, and Pb, even higher than those values included in SQGs. More studies are necessary in the area to clarify the sources of these metals and to establish if control measurements would be required in the area.

CONFLICT OF INTEREST

None declared.

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